TEXTBOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.SC., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., PH.D., F.I.C., F.R.S.

SPECTROSCOPY

SPECTROSCOPY

BY

E. C. C. BALY, C.B.E., M.Sc., F.R.S.

GRANT PROFESSOR OF INORGANIC CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL
FELLOW OF UNIVERSITY COLLEGE, LONDON

IN TWO VOLUMES

VOL. I

WITH ILLUSTRATIONS

THIRD EDITION

LONGMANS, GREEN AND CO.

39 PATERNOSTER ROW, LONDON, E.C. 4

NEW YORK, TORONTO

BOMBAY, CALCUTTA AND MADRAS

1924

5

Made in Great Britain

PREFACE TO THE THIRD EDITION.

THE science of Spectroscopy during recent years has advanced to a remarkable extent. Since the last edition was printed new fields of investigation have been opened up and the limits of knowledge in the older fields have been pushed very far forward. It has not been possible to comprise within one volume any account, however brief, of the whole, and it has therefore been decided to divide the book into two volumes. The present volume deals with the standard methods of work in the infra-red, visible, and ultra-violet regions of the spectrum, and thus includes the first half of the original volume.

I have endeavoured to present the subject in such a way that it may be of assistance to those who wish to undertake work in Spectroscopy, although this involves some danger since everyone who has himself worked in a field finds it difficult to avoid the viewing of that field from his own particular angle. Fully conscious of my inability to do real justice to the subject I trust that any shortcomings may be kindly criticised, for they have had their origin not in the want of a true love for the science but rather in the selections I have made from the great wealth of fascinating material.

Once again I have to record my gratitude to many friends who have rendered me most valuable help. These are too numerous to mention, but I would refer especially to three. To Miss E. E. Kelly I owe much for her untiring assistance in lightening the labour involved in the compilation of this book. To Professor J. N. Collie and Professor F. G. Donnan I am more indebted than I can possibly say. To the inspiring personality of each of these philosophers, to their never-failing wealth of kindly criticism and help, to their profound power of encouragement when the days seem dark, to their stimulating enthusiasm for Dame Nature and her handiwork, I owe a debt that can never be repaid.

E. C. C. B.

THE UNIVERSITY, LIVERPOOL,
February, 1924.

PREFACE TO THE SECOND EDITION.

SINCE the first edition of this book appeared there have b(published a very great number of papers describing most i portant investigations in Spectroscopy. The advance of reseai in this subject during the last six or seven years has b(exceptionally great, and I have found it exceedingly diffic satisfactorily to deal with this work and still to keep the bo within reasonable limits. Even with the increase in size I canr but feel that I have done scant justice to most valuable a striking investigations. I have endeavoured, however, as far possible to give a *resumé* of the salient points of the more mode work, and I have also ventured to add at the end of the releva chapters a list of references to the literature which I trust m: prove of value to those who wish to read up the various subjec in greater detail than I have been able to include in the text.

I tender my most cordial thanks to those kind friends wl took the trouble to send me notes on the inaccuracies and mi prints that were present in the first edition. I would especial in this connection thank Mr. H. M. Reese of the Columbia Ur versity for his most valuable assistance.

To many friends am I indebted for their direct help in tl preparation of this new edition. Amongst these I must mentio two, Mr. P. A. Baldock, B.Sc., who was kind enough to undei take the photographs of spectra which have been included, an also to Miss W. Judson, B.Sc., to whose keen interest and har work I am more indebted than I can say. My readers may fin reason to thank Miss Judson in the extensive index which she ha prepared, and which I feel sure will prove a valuable adjunct t(the book.

E. C. C. B.

THE UNIVERSITY, LIVERPOOL,
March, 1912.

PREFACE TO THE FIRST EDITION.

IN the following pages I have endeavoured to present the subject of Spectroscopy from the practical side. As full details as possible have been given of the methods of working with the various types of instruments. In the many branches of Applied Spectroscopy, as distinct from the statistical work, it has been quite impossible to deal with the great number of researches of the present time. Typical Investigations have, therefore, been selected, both with the view of indicating the lines upon which present work is being carried on, and, further, in the hope, which I trust is not a vain one, that more workers may be encouraged to enter this fascinating and prolific field of research.

I have given no set tables of wave-lengths, because these tables are published in a most convenient form by Dr. Marshall Watts, and their inclusion would have necessitated the sacrifice of a considerable amount of the text.

My thanks are due to the many authors who kindly have allowed me to reproduce drawings and illustrations from their publications. To Professor Ames, of the Johns Hopkins University, am I particularly indebted for placing at my disposal the drawings and descriptions of the Rowland grating ruling engines. I am also indebted to Professor Kayser's *Handbuch der Spectroscopie* for information upon his work with Professor Runge on Spectral Series, and the work of the latter with Professor Paschen on the Zeeman effect. I have also to record my cordial thanks to my friends who have given me much valued help—Mr. H. J. Harris, Professor F. T. Trouton, Messrs. J. K. H. Inglis and A. W. Porter.

E. C. C. B.

UNIVERSITY COLLEGE, LONDON,
April, 1905.

CONTENTS.

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

PLATE

SPECTROSCOPY.

CHAPTER I.

HISTORICAL.

THE foundation of spectroscopy may be traced in the discovery by Sir Isaac Newton, in the year 1666, that the amount of refraction suffered by different coloured rays of light is different with the same medium. He proved this, in the first place, by looking through a glass prism at some pieces of red and blue paper, when he noticed that the relative positions of the different coloured pieces appeared to be altered. In the second place, Newton soon afterwards showed that a ray of sunlight is a combination of a number of rays of various colours, each of which suffers a different amount of refraction or bending on being made to pass through a glass prism, and that of these rays the red is least and the blue most refracted. The historical experiment actually carried out by Newton is familiar to every one, in which he caused a pencil of sunlight, which was admitted through a round hole in the shutter of a dark room, to pass through a glass prism and then fall on a screen. He thus obtained what he called a spectrum, that is, an orderly arrangement of a series of coloured images of the hole in the shutter, these coloured images appearing in different positions by virtue of the different amount of refraction suffered by rays of various colours. Before Newton had carried out these experiments, the colours produced by the passage of white light through a prism were supposed to be produced in the prism, for, up till that time, people had imagined that the white light was actually changed into the different colours.

The phenomenon of the refraction of light and the laws connected therewith were, of course, well known in Newton's time, having been first discovered by Snell in 1621, and further worked out and first published at a later date by the great philosopher Descartes. Although both Snell and Descartes were unaware of the composite nature of white light, they succeeded in proving the existence of a constant relation between the angles when light is refracted; and Newton, as the result of his discovery that white light is a mixture of many different colours, was able to extend the applicability of the Snell and Descartes relation, and show that, while it differs for rays of different colours, it is constant for rays of the same colour.

Now, the paths of light rays through isotropic media always lie along straight lines, that is to say, they travel with a constant velocity; the

velocity depends on the nature of the medium. When light passes from one isotropic medium into another it suffers generally a change in velocity, and this change tends to cause a change in direction, the new path being a straight line at some angle with the first path. This bending of the path of the rays is called refraction, and the angular measure of the amount of bend is called the angle of deviation. This angle of deviation varies with the inclination at which the rays fall on to the boundary surface between the two media. It has a zero value when the rays fall perpendicularly on to this surface, and tends towards a maximum the more obliquely they fall. The amount of deviation suffered by a ray of light in passing from one medium to another depends upon the relative velocities of light in the two media and the angle at which the ray falls on the boundary surface.

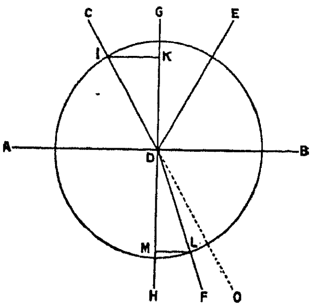


FIG. 1.

The following laws were found by Snell and Descartes to hold good for all cases of simple refraction.

The incident and refracted rays lie upon opposite sides of the normal to the boundary or refracting surface at the point of contact, and the normal and the incident and refracted rays lie in the same plane.

The sines of the angles of incidence and refraction bear a constant relation to one another—a relation which is solely dependent upon the nature of the two media (Snell's law).

These laws will be better understood from a particular case. In Fig. 1 let the straight line AB mark the separation between any two isotropic media; for example, let AB represent a surface of water; and further, let a ray of light, CD, strike this water surface at the point D.

This ray, therefore, at the point D will be divided into two portions, one of which is reflected off in the direction DE, thus continuing its path in the first medium, air, while the other portion enters the water and pursues the path DF. This path DF is not a continuation of the path CD, but is refracted from it to some extent, and if CD be continued to O, the amount of the bending is shown by the angle FDO, which is the angle of deviation.

Through the point of incidence D the straight line GDH is drawn normal to the refracting surface, and this gives the angle of incidence CDG and the angle of refraction FDH.

Now the first law of refraction states that the refracted ray DF always lies on the opposite side of the normal GH to the incident ray CD, and, further, that the two rays CD and DF lie in the same plane as the normal GH. To find the relation, stated in the second law, between the angles of incidence and refraction, draw any circle with D as centre, and from the points where this circle cuts the incident and refracted

rays, draw the straight lines IK and LM perpendicular to the normal GH.

Now, the sine of the angle CDG is equal to $\frac{IK}{ID}$, and the sine of the angle FDH is equal to $\frac{LM}{LD}$, and therefore, if the angles CDG and FDH be called i and r respectively—

$$\frac{\sin i}{\sin r} = \frac{\frac{IK}{ID}}{\frac{LM}{LD}} = \frac{IK}{LM}, \text{ since } ID = LD.$$

Snell's law states that the ratio $\frac{\sin i}{\sin r}$, or $\frac{IK}{LM}$, is constant for the same pair of media, whatever the value of i may be. This ratio is called the index of refraction, and is usually denoted by the symbol n.

If the incident ray is normal to the surface, then the angle i is zero, and therefore, since $\sin 0° = 0$, the angle r is also zero; this means, of course, that no refraction takes place, and the ray passes straight into the new medium.

It is important to notice that the index of refraction is a relative term depending on the two media; for example, in the above case it is a measure of the ratio of the velocities of light in air and in water; in general, by the index of refraction of a substance is always meant, unless specially noted to the contrary, the ratio of velocities of light in air and in the substance. The term "absolute index of refraction" refers to the value obtained with the specified substance in a vacuum and is given by the product of the observed index into the refractive index of air for the particular light ray employed.

The direction in which the refraction of the light takes place as a general rule depends upon the densities of the two media, and, although there are exceptions, it generally follows that, when a ray of light enters a dense medium from a rare one, it is refracted towards the normal, and conversely when passing from a dense into a rare medium it is refracted away from the normal. This is the case with the example shown in Fig. 1, where the light enters a denser medium and is refracted towards the normal; exceptions to this are known, as, for example, certain oils, which, though they are less dense than water, have a higher index of refraction than water, and, therefore, the velocity of light in them is less than in water.

It is interesting to consider more fully the simple case of refraction shown above in Fig. 1, because certain important results can be obtained from it. If the index of refraction for two media be known, the different values of the angle of refraction resulting from different angles of incidence may readily be calculated with the help of a book of mathematical tables. This may be done for air and water, assuming the index in this case to be 1·34, which is sufficiently accurate for the present purpose.

By Snell's law we have—

$$\frac{\sin i}{\sin r} = 1{\cdot}34,$$

$$\text{and } \sin r = \frac{\sin i}{1{\cdot}34}.$$

From this it is possible to calculate the different values of r when i is given different values, and these are set forth in the following table:—

TABLE I.

Angle of incidence.	Angle of refraction.
0°	0° 0 0″
10°	7° 29′ 0″
20°	14° 51′ 48″
30°	22° 1′ 27″
40°	28° 49′ 26″
50°	35° 4′ 0″
60°	40° 30′ 20″
70°	44° 48′ 41″
80°	47° 36′ 45″
90°	48° 35′ 25″

In the column headed angle of incidence are given values of this angle, increasing by 10° from 0°, or normal incidence, to 90°, when the incident ray lies along the surface of the water, while in the second column are given the corresponding values of the angle of refraction. Since the angle of incidence cannot have a greater value than 90°, it follows from the table that, in the case of air and water, the largest possible value of the angle of refraction is 48° 35′ 25″.

Let us now consider the converse case of the light passing from water into air, and let AB in Fig. 2 again represent a boundary surface between air and water. The incident ray CD now strikes this surface from the water, and again, as before, is divided into two portions, one of which is reflected from the surface along the path DE, while the other leaves the water and follows the path DF, and, since the air is less dense than the water, DF is refracted from the normal. The relations given in Table 1 evidently hold good in this case, and by their means it is possible to follow the changes produced in the angle FDG when changes are made in the angle CDH; for example, when the angle CDH has a value of 40° 30′ 20″, the angle FDG measures 60°, and so on. If the angle CDH be increased until it reach the value 48° 35′ 25″, the angle FDG will become equal to 90°, and therefore the emergent ray will lie along the surface of the water. Now, 90° is evidently the largest possible value of the angle GDF, so that, if the angle CDH be increased beyond the value of 48° 35′ 25″, none of the light will be able to leave the water at all, but the whole will be reflected along the path DE. This is true for any two media, and thus we have the result that light cannot pass out

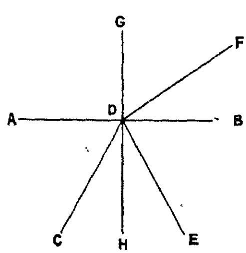


FIG. 2.

from a dense medium into a light medium, but is totally reflected when the angle of incidence exceeds a certain definite value, which, in the case of water and air, has been shown to be $48° 35' 25''$.

This particular value of the incident angle is called the *critical angle*, and can, by Snell's law, very readily be calculated for any two media when the relative value of the index of refraction is known. In the equation $\frac{\sin i}{\sin r} = \frac{1}{n}$, it is only necessary to put $r = 90°$, for it has been shown that i reaches the critical value when $r = 90°$.

Therefore, since $\sin 90° = 1$,

$$\frac{1}{\sin i} = n, \text{ and } \sin i = \frac{1}{n}.$$

For example, the refractive index of a particular glass is 1·62, and therefore $\sin i = \frac{1}{1{\cdot}62} = 0{\cdot}6187$, from which i is found to be $38° 13' 30''$, which is the critical angle for the glass in question.

The greater the value of the index the smaller is the critical angle, and it is interesting to note that the brilliance of a diamond in a deep setting is due to the very small value of the critical angle, which is about $19° 30'$, so that all the light which reaches the bottom surface at a greater angle than this is totally reflected, with the result that much less light passes out through the bottom than would be the case with glass or similar substances.

The following points must be remembered in connection with the simple refraction of light:—first, that a certain quantity of the light is always reflected, and in no case can total refraction occur; and second, that no refraction from a dense into a rare medium can take place unless the angle of incidence is less than a certain critical angle the sine of which is equal to the reciprocal of the index of refraction.

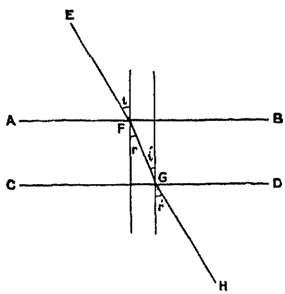


FIG. 3.

In the cases previously considered the refraction at a single boundary surface only has been dealt with; it is, of course, necessary to deal with two boundary surfaces at least for any practical purpose. The simplest case is that of the passage of a beam of light through a medium with parallel surfaces, such as a plate of glass; this is shown in Fig. 3.

Let AB and CD represent the upper and lower parallel surfaces of a piece of plate-glass, and let the ray EF fall on the surface AB, making an angle of incidence i. Part of the ray enters the glass, being refracted towards the normal, and pursues the path FG, making the angle of refraction r. By Snell's law, therefore—

$$\frac{\sin i}{\sin r} = n.$$

Again, the ray FG on reaching the lower surface CD is divided into two parts; one of which is reflected and the other passes out into the air, being refracted from the normal. By Snell's law, therefore, again—

$$\frac{\sin r'}{\sin i'} = n.$$

It follows that—

$$\frac{\sin i}{\sin r} = \frac{\sin r'}{\sin i'}.$$

But by construction the angle i' is equal to the angle r, and therefore the angle r' must be equal to the angle i.

The refraction at F and G is, therefore, equal, but in opposite directions, so that the ray of light on emerging into the air from the glass pursues a path parallel to its original path; a plate of glass with parallel sides, therefore, when introduced into the path of a beam of light, in no way alters the direction of the path.

The case is different, however, when the two boundary surfaces are not parallel to one another, but are inclined at some angle to one another. The deviation in the path of a ray of light produced by the refraction at the first surface is not counteracted at the second surface, but is always increased. For example, let us take the case of a prism.

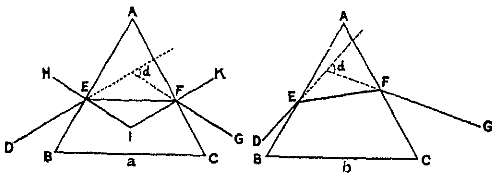


FIG. 4.

Let AB and AC in Fig. 4 represent the refracting surfaces of the prism ABC, which are inclined together at the angle BAC. Then, if the ray DE fall on the surface AB, making an angle of incidence DEH, part will enter the prism and follow the path EF, which makes an angle of refraction FEI. The relation between the angles DEH and FEI is defined by the value of the index of refraction. The ray EF on reaching the second surface AC is refracted away from the normal and passes along the path FG, the relation between the angles GFK and EFI being also defined by the index.

It is evident that the deviation in the path of the ray DE, produced by the refraction at the first face, is increased still more by that which occurs at the second face; the total deviation, which is the sum of the deviations at the two surfaces, is shown by the angle d, which is obtained by prolonging the paths of the incident and emergent rays. It will readily be seen on reference to the two cases shown in Fig. 4 that the angle d has the lesser value in case a; indeed, it can be proved that the total deviation is the least possible when the ray passes symmetrically

through the prism, that is to say, when the angle DEB is equal to the angle GFC. When, therefore, a ray of light passes symmetrically through a prism, the deviation is a minimum; it is important to notice that, in the case of minimum deviation, the path of the rays inside an isosceles prism is parallel to the prism base (BC in Fig. 4).

In the cases of refraction dealt with in the preceding pages a tacit assumption was made that the rays of light were homogeneous, that they consisted of light of only one colour; but since Newton, by his discovery of the composite nature of white light, showed that rays of different colours suffer different amounts of refraction, it becomes necessary to take a wider view of the phenomena. While Snell's law states that the value of the index of refraction is a constant for rays of one colour, it differs for rays of different colours, and Newton as a result of his experiments found that the value of n for red light is smaller than the value for blue light, or, in other words, that red light suffers less and blue light more refraction with the same medium. The fact of Newton obtaining a spectrum is simply explained, as shown in Fig. 5.

Let ABC represent a prism and DE an incident pencil of white light. The refraction at the point E will of necessity be different for every ray of different colour in the pencil, and, therefore, every ray will pursue a different path through the prism; three such rays are shown in the figure EF, EG, and EH. All the rays are again refracted at the second face, and their paths become still more divergent, as shown for the three rays FI, GK, and HL. The different colours are thus all separated by the prism, and if they were received on a screen a band of colours would be produced, in which each colour would be placed according to its index of refraction; for example, the blue would appear at the end nearer the base of the prism, *i.e.* at L, while the red would appear at the other end, I, while the mean position would be occupied by green.

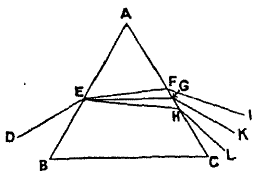


FIG. 5.

The indices of refraction for light of different colours have been measured for many substances and these measurements are of great significance in spectroscopy. In the first place, they are important with reference to the use of prisms and lenses in spectroscopes, and in this connection they will be discussed more fully in Chapter III. In the second place, the refractive indices of a substance are intimately connected with its powers of absorbing light, and this will be dealt with under absorption spectra in Volume II.

A typical example of the indices for a glass with rays of different colours may be given to show the variations in their values—

	n
Red light	1·612
Yellow light	1·615
Green light	1·619
Blue light	1·623
Violet light	1·631

Now, Newton, in his investigations on the spectrum, did not advance beyond the point indicated, in spite of the fact that he finally came to use a lens between the opening and the prism. It is evident that by this means he obtained better definition than before. On consideration it follows that, if purity of spectrum be desired, the most satisfactory source of illumination will be a narrow slit; for a slit will tend to eliminate all unequal overlapping of its coloured images, and, therefore, to improve greatly the quality of the spectrum. Newton recognized this, and in his later experiments he replaced the round opening by a slit, but in spite of this he did not advance any further. The reason of this appears to lie in the fact that his prisms were of a very poor quality, with the result that the definition was far from satisfactory. Newton failed to notice that the light from the sun is not perfectly homogeneous, and it was Wollaston who first discovered this by observing the rays of sunlight admitted through a narrow slit in a window blind. Wollaston then noticed a number of black lines, which crossed the spectrum in a direction parallel to the slit. For some reason he did not investigate these lines further, and it was reserved for Fraunhofer, the celebrated optician of Munich, to study them thoroughly, and point out their immense importance—an investigation which laid the foundation-stone of the modern science of spectroscopy.

Fraunhofer first occupied himself in greatly improving the apparatus for studying the spectrum, for, instead of allowing the rays to pass directly through the prism and fall upon a screen, he interposed a convex lens between the slit and the prism, and thus projected the images of the slit on to the screen; he obtained in this way a well-defined spectrum, which showed the black lines very well marked. He also made use of a telescope to examine the spectrum visually, and was able in this way to investigate the phenomena of the black lines more thoroughly. By the use of different prisms and by varying the form of his apparatus, Fraunhofer was able to prove that the black lines have perfectly fixed positions in the solar spectrum, and he therefore concluded that the light which we receive from the sun, although it is to all intents and purposes white, does not give a complete spectrum, but is deficient in certain rays, and that these deficiencies are marked by black spaces in the spectrum. Although the actual meaning of the phenomenon was not known to Fraunhofer, he foresaw the great importances of the lines as landmarks, so to speak, by means of which it would be possible to make accurate measurements of the refrangibility of the different coloured rays. In his investigations, Fraunhofer mapped about seven hundred of these lines, and labelled the eight chief and most decided of them by the letters of the alphabet, beginning in the red with A, and ending in the violet with H. At the present time these lines are still called the Fraunhofer lines, with the original letters attached, though the lettering has been very considerably extended beyond the limits of the spectrum which Fraunhofer investigated. It may readily be understood, since the spectrum of pure white light consists of a series of bright images of the slit in juxtaposition to one another, that if the light of the sun is deficient in certain rays the

bright images of the slit corresponding to those rays will be absent from the spectrum which will then exhibit dark "lines" at certain definite points. It is of some interest to note how the term "spectrum line" has been universally adopted in spectroscopy, the term being of course synonymous with "light ray."

This constituted the first part of Fraunhofer's work; the second part was connected with an investigation into the possibilities of measurement of the actual length of the waves of light, in which he succeeded in developing the theory of interference of light so far as to invent and construct for himself the first grating, by means of which he made several measurements of the wave-length of the D line with a wonderful degree of accuracy. The method Fraunhofer used for measuring the wave-length of light by means of a grating is indeed the same as that of the present day; but before entering into a description thereof, it is advisable to consider the work which had been previously carried out on the diffraction and interference of light upon which the method is based.

It was first noticed by Grimaldi in 1665 that a ray of light as it passes by the edge of some opaque object suffers a certain amount of bending, or diffraction as he called it; in other words, the shadow cast by the

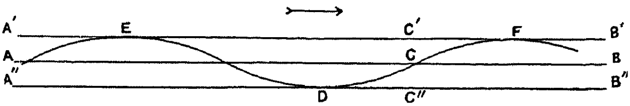


FIG. 6.

sharp edge of an opaque body is not necessarily absolutely sharp. For example, when a beam of white light passes through a slit and is allowed to fall upon a screen, the image of the slit formed thereon is seen to be surrounded by coloured bands. Grimaldi also observed that, under certain conditions, when light is received upon a screen from two adjacent sources, darkness is produced, and he stated, though the meaning was not clear to him, that light added to light can produce darkness. Many years afterwards the subject was thoroughly worked out by Thomas Young and by Fresnel, the former of whom in 1801 published the famous principle of interference; these physicists showed that the Grimaldi experiment and many cognate phenomena can be very clearly explained by the wave theory of light. This theory, first developed by Huyghens in 1678, supposes that light consists of transverse vibrations in an all-pervading medium, called the ether—that is to say, vibrations analogous to those of a stretched string, in contradistinction to sound waves, which are longitudinal. As an illustration, a single ray of light may well be compared to a series of waves passing along a stretched string of very great length, of which let a portion be represented by the curved line in Fig. 6.

The string in a state of rest would lie along the straight line AB, but when in a state of vibration—that is to say, under the influence of a system of waves passing along its length—it assumes some such shape as

is shown by the curved line. The limits of the wave motion are evidently given by the line A′B′ on the upper side, and by A″B″ on the lower side. The direction of propagation of the waves is assumed to be in the direction of the arrow, *i.e.* from left to right. If now any one particle of the string be considered, it will be seen that, during the passing of the waves, it simply moves to and fro in straight lines between the limits given by A′B′ and A″B″. For instance, let us consider the particle C in the figure; evidently this will move to C″ as the bottom of the wave passes, and then travel to C′ when the top of the wave passes, and finally will return to C—this cycle representing its motions during the passage of a complete wave. Thus, a whole wave-length is represented by the length AC, and in speaking of a whole wave-length of light the complete length from A to C is meant. Every other particle of the string is executing exactly similar motions, though these are not necessarily in the same direction at the same time as those of the particle at C, as, for instance, the particles at D and E. The particle at A, however, performs exactly the same movements simultaneously with C, and in like manner the motions of the two particles at E and F are synchronous. Since both A and C, and E and F are separated by one whole wave-length, it follows that particles one or more whole wave-lengths apart execute the same movements simultaneously; such particles are said to be in the same phase. Similarly, particles which are separated by one or any odd number of half wave-lengths, such as E and D, are said to be in opposite phase—that is to say, at any moment they are moving with the same velocity, but in opposite directions.

The case of light waves travelling through the ether is similar to the above; the ether particles, if we may so speak, separated by any even number of half wave-lengths, are always in the same phase, whilst those separated by any odd number of half wave-lengths are always in opposite phase.

We have yet, however, to take account of the undoubted, though small, bending or diffraction that a ray of light suffers as it passes an opaque object such as was first noticed by Grimaldi. Now Huyghens, in considering the means of propagation of light through the ether, laid it down as a general axiom that each ether particle in a state of vibration becomes the source of a new system of vibrations. At any given moment, therefore, every particle in the front surface of a wave acts as the source of a new system of waves, and the combined effect of these disturbances on the adjacent particles after unit time forms the new wave front. It was assumed by Huyghens that these secondary waves, as they may be called, act entirely in the direction of propagation of the main wave; this however is not strictly true, although a maximum effect is produced in the direction of propagation. On these theoretical considerations Grimaldi's diffraction and Young's interference experiments can be explained.

One of the experiments carried out by Young in extension of Grimaldi's original work was to cause the light from two closely ad-

jacent sources to fall upon a screen, and he then found that when white light was used fringes of colour were produced, and alternating light and dark bands in the case of homogeneous light. The explanation of this phenomenon of what are called interference bands follows directly from the wave theory of light, as was shown by Young when the combined effect of two rays coming from different directions on an ether particle is considered. If the two disturbances be equal in amplitude and reach the ether particle in the same phase, both will tend to move the particle in the same direction, and consequently its motion will be doubled and a quadrupling of the light at that spot will ensue. If, on the other hand, the two disturbances be in opposite phase, one will tend to move the particle in one direction, while the other will tend to move it in the opposite direction with an equal force; the result will be total extinction at that point. Such conditions are obtained in Fig. 7, where A and B are supposed to be two points emitting light of one colour and in the same phase; they must each, therefore, be considered to be a source of a system of waves which are continually expanding in every direction around them. At any given moment waves which started from A and B at the same instant must have travelled the same distance, and a small portion of each wave may be represented by the sets of circles X_1X_2 and Y_1Y_2, X_1X_2 having B and Y_1Y_2 having A as origin, for each set is described with B and A respectively as centres and with equal radii. Each set of circles may be taken to represent one whole wave, that is to say, the two thick circles in each case are one whole wave-length apart, and the two thin circles are a half wave-length distance from the two thick ones in each set. It follows, therefore, that the ether particles lying on all of the four thick circles are always in the same phase of vibration, and that the particles lying on the thin circles are in opposite phase to those on the four thick circles, but are in equal phase amongst themselves. The intersections of these circles mark the points where the ether particles come under the influence of disturbances from both A and B at the same instant; it is the effects produced at these points that must be considered.

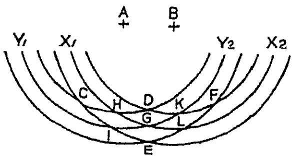


FIG. 7.

At the intersection of the four thick circles at the points C, D, E, and F, the ether particles are simultaneously subjected to two equal disturbances at the same phase, and therefore a spot of quadruple brightness occurs at these places; the same is to be noticed at G, where the two thin circles intersect. At the points H, I, K, and L, on the other hand, where the thick and thin circles intersect, the ether particles come simultaneously under the influence of two equal disturbances at opposite phase, and therefore spots of total blackness are produced.

It is important to notice in connection with this phenomenon of the interference of light, as it was named by Young, that no loss of energy

takes place; the light is distributed in maxima and minima, but the total quantity remains the same, that which is wanting in one place appears in another.

The actual experiment carried out by Young is satisfied by an exactly similar explanation to the above, because he used two sources of light placed very near together, which emitted light at equal phase. He arranged this by allowing a ray of sunlight from a hole in a shutter to illuminate a second screen which was perforated by two small holes very close together; where the images formed by these two holes overlapped upon a third screen, he obtained the interference bands. Now, these two small holes are directly comparable to the sources of light A and B in Fig. 7, for the light which passed through them both was supplied by the single hole in the first shutter, and was, therefore, evidently all of the same phase.

It is of importance to calculate the position of the light and dark bands obtained in this experiment of Young's, because it is possible to make rough measurements of the wave-length of light by its means. In Fig. 8 A and B are the two pinholes which are emitting homogeneous light at the same phase, and C is the screen on which the bands are formed. Let us now consider the illumination of the screen C at any point, F; evidently the straight lines AF and BF will represent the paths of the rays of light arriving at F from A and B respectively. With centre F and radius FA the small arc AG is described from A to the line BF; the length BG, therefore, represents the difference in path travelled by the two rays BF and AF in their journey between the two screens; evidently the waves from the aperture B travel a greater distance than the waves from A, the difference in path being given by the length BG. If now BG is equal to any even number of half wave-lengths, it follows that the waves leaving A and B in the same phase arrive at F in the same phase, and therefore the illumination at F is quadrupled. If, on the other hand, BG be equal to any odd number of half wave-lengths, the waves will arrive at F in opposite phase, and total extinction will occur. The same holds good on the other side of the centre E, and since, of course, E itself marks the position of a bright band, the effect is produced of a central bright band surrounded by alternate minima and maxima of brightness, the minima occurring when BG equals 1, 3, 5, etc., half wave-lengths, and the maxima when BG equals 2, 4, 6, etc., half wave-lengths.

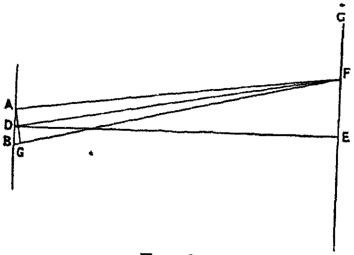


FIG. 8.

It is possible by means of this experiment to make a rough determination of the wave-length of the light, since we can calculate the value of BG by means of measurements which are quite simply obtained. In Fig. 8 the points F and D are joined by a straight line; then, since

the arc AG is very small, it may be considered as a straight line at right angles to DF, and further, since AB is perpendicular to DE, it follows that the angle BAG is equal to the angle FDE—

Therefore $$\frac{BG}{AB} = \frac{FE}{FD}, \text{ and } BG = \frac{FE \times AB}{FD}.$$

Now, in an actual experiment the length FE is very small compared with the distance between the screens, and therefore FD is very little longer than DE, so that we may substitute DE for FD in the above equation without introducing any appreciable error. We have, therefore—

$$BG = \frac{FE \times AB}{DE}.$$

The distances FE, AB, and DE can easily be measured, and thus the length BG can very simply be obtained. It must be remembered that, when F is taken as the centre of a bright band, BG is equal to some even number of half wave-lengths, two if the first bright band be

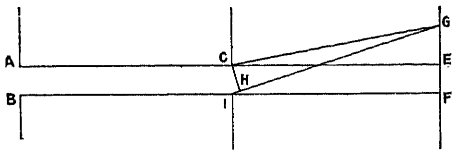


FIG. 9.

measured, four with the second, and so on; and similarly, when F is taken as the centre of a dark band, BG is equal to some odd number of half wave-lengths, one in the case of the first band, three in the case of the second, and so on.

By an extension of this principle of interference the phenomenon can be explained which was first observed by Grimaldi, and called by him diffraction of light, namely, the appearance of coloured bands round the shadow cast under certain conditions by an opaque object. The true explanation of this phenomenon is due to Fresnel, who thoroughly investigated the subject, and showed that all the observations could be accounted for by Huyghens's principle and Young's theory of interference. The most satisfactory results are obtained when a beam of light from a narrow slit is allowed to pass through a second slit parallel to the first and then to fall on to a screen; on each side of the central image and parallel to it well-developed fringes are to be seen, which consist of coloured bands when white light is used, and of alternate bright and dark bands when the light is homogeneous. The explanation of these fringes follows very clearly from what has gone before, as may be seen from Fig. 9, which is a diagrammatic representation of the experiment.

AB and CI are the two parallel slits, and EF the central image, formed on the third screen by the beam of light passing directly

through the two slits. By the use of the two slits we are enabled to ensure that all the waves of light leaving CI for the third screen are in the same phase, that is to say, that all the ether particles lying between C and I are in the same phase of vibration; let us now for the present assume that the experiment is made with light consisting entirely of rays of the same wave-length. It follows from Huyghens' theory of the propagation of light that the ether particles lying between C and I become sources of disturbances, which, although their maximum effect is in the direction of propagation of the light, *i.e.* towards EF, yet proceed also in every direction on each side of the central beam. The third screen, therefore, becomes illuminated on either side of the central image; a certain amount of interference, however, takes place amongst these rays, an amount which varies at different points. The central image EF is necessarily very bright for two reasons, the first because the maximum effect of the vibrations of the ether particles between C and I tends directly towards EF, and the second because a minimum of interference occurs at this place. In order to deal with the illumination on each side of the central image let us consider that produced at some point, G, on the screen. The straight lines GC and GI are drawn, and these will evidently include all the rays which arrive at G; it is with the mutual interference of these rays that we are concerned. If with centre G and radius GC the arc CH be drawn, the distance IH will represent the difference in path travelled by the two outside rays IG and CG in their journey to G. When this length IH is equal to any odd number of half wave-lengths, the two outside rays of the pencil arrive at G in opposite phase and neutralise one another; the next pair also interfere with one another, but not entirely, since they do not arrive at G in exactly opposite phase; the next pair again interfere still less, and so on until the ray in the centre is not interfered with at all. Under these circumstances the total amount of interference at G is the least possible, and G therefore marks the position of a bright band. When, however, IH is equal to any even number of half wave-lengths, and the two outside rays arrive at G in equal phase, then there must meet at G an equal number of rays at opposite phase; evidently the two halves of the pencil will neutralise one another, and in this case G will mark the centre of a dark band. When, therefore, homogeneous light is used there occurs on each side of the central image a series of dark and bright bands the positions of which depend upon IH being equal to any even and odd number of half wave-lengths respectively. A very rough measurement of the wave-length of the light is also practicable with this experiment in a similar way to that shown before with Young's interference experiment with two adjacent pin-holes.

If white light had been used in the above instead of homogeneous light, coloured bands would have been obtained in place of the alternate bright and dark bands; the explanation of these follows on exactly the same lines as that given for homogeneous light. The point G has already been shown to mark the centre of a bright band when IH equals an odd number of half wave-lengths, and thus, if the light emanating from

the ether particles between C and I be a mixture of disturbances of many different wave-lengths, there will be of necessity many positions of G at which the light is brightest—a different one for every ray of different wave-length. Instead of a bright band of one colour, as in the case of homogeneous light, a row of very closely situated maxima of different colours will be obtained, *i.e.* a spectrum, in which the colours are placed according to their wave-lengths. Since violet light has the shortest wave-length this colour will appear on that side of each band which is nearer the central image, and the red, which has the longest wave-length, will appear on the outer side or that which is further from the central image. In place of the bright and dark bands which are obtained with homogeneous light, series of spectra are now observed with their violet ends turned towards the central image; and of these spectra the first satisfies the condition that IH is equal to one half wave-length, the second the condition that IH is equal to three half wave-lengths, and so on. These spectra decrease in brightness the further they are from the central image, owing to the fact that the effect of the disturbances due to the ether particles between C and I is a maximum in the direction of propagation, and decreases rapidly when the angular distance from this is increased.

In connection with the use of the two terms "diffraction" and "interference," it is important to notice the difference between them; interference is used in reference to those cases in which the mutual action of two or more direct pencils of light is concerned, whilst the term diffraction is only applied to the case when an actual bending of the rays occurs, and Fresnel's extension of Huyghens' axiom is made use of in the proof of the resulting phenomena.

The application of diffraction methods to the study of spectra was made by Fraunhofer, who so far developed them that he was able by their means to make accurate measurements of the wave-length of light. Fraunhofer conceived the idea of using in place of the single slit, as was dealt with in the last case, a number of such apertures placed at an equal distance apart. He collected all the diffracted rays from these apertures with a convex lens, and examined the spectra produced at the focus of this lens. This series of equal and equidistant apertures is called a grating, and it is interesting to note that in devising this apparatus Fraunhofer invented the method of determining wave-lengths by gratings as used at the present time.

A diagram of the apparatus is shown in Fig. 10. Only two of the apertures AB and CD have been drawn, which are sufficient to explain the theory, and L is a convex lens called the collimator, which is used to throw a parallel beam of light from S upon the grating; S is a slit placed parallel to the grating apertures and illuminated from some outside source. The lens used for collecting and bringing to a focus the rays which pass through the grating apertures is not shown on the diagram, there being no need for it as far as the theory is concerned, because it in no way alters the phase of vibration of the waves.

Now the ether particles lying in the apertures AB and CD become

sources of vibrations which proceed chiefly in the line of propagation towards M_1, M_2, M_3, and M_4, but also in other directions, for example, towards X_1, X_2, X_3, and X_4. When these rays are brought to a focus by means of the convex lens, evidently those travelling towards M_1, etc., will produce a bright image of the slit S without any mutual interference taking place, but the case is different with the diffracted rays X_1, etc. In order to investigate the conditions of mutual interference among the latter, the straight line BE is drawn perpendicular to DX_4, when the length DE will represent the difference in path travelled by the two outside rays DX_4 and BX_2, and also by the two outside rays CX_3 and AX_1, and therefore also the difference in path travelled by every pair of corresponding rays in the two pencils. If now DE is equal to any odd number of half wave-lengths, it follows that for every ray in one pencil there is a corresponding ray in the other pencil at opposite phase, and therefore total interference takes place when the rays are combined at the focus of the lens. The same manifestly holds good for every adjacent pair of apertures of the grating.

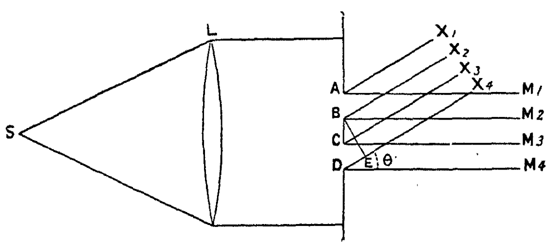


FIG. 10.

Again, if DE be equal to any even number of half wave-lengths, then the reverse will be the case, for every corresponding ray in the two pencils will be at equal phase, and therefore the rays from these two apertures and every adjacent pair will combine at the focus of the lens to give a bright image of the slit.

It is, of course, very possible that DE be not equal to either an odd or even number of half wave-lengths; in such a case interference takes place, not between the diffracted rays from adjacent apertures, but between those from apertures which are some way apart. For example, let us suppose DE to be equal to one-hundredth of a wave-length, then the rays from the first and fifty-first apertures mutually interfere, similarly those from the second and fifty-second, and so on. It can therefore readily be understood from this that, provided there be sufficient apertures, complete interference always takes place except when DE is equal to an even number of half wave-lengths.

In the case of complex light, which consists of waves of many different lengths, there are just as many values of DE, with which a bright image of the slit is produced, and, as each of these has a different colour, a spectrum is produced in which each colour is distributed strictly ac-

cording to its wave-length. We have, therefore, produced on each side of the central image a first spectrum, which corresponds to the condition that DE is equal to two half wave-lengths; and then, outside of this first spectrum, a second, which corresponds to the condition that DE is equal to four half wave-lengths; and again, outside this, a third, and so on. These spectra are called respectively those of the first, second, third, etc., orders, these being the names which were given by Fraunhofer.

The appearance of the spectra as obtained with a grating is shown in Fig. 11, in which O represents the undiffracted central image.

It often happens that the different orders overlap one another, as is shown in the figure in the case of the second and third orders.

Now, although the length DE in Fig. 10 cannot be measured, it may be very simply arrived at from measurements which are very easily carried out.

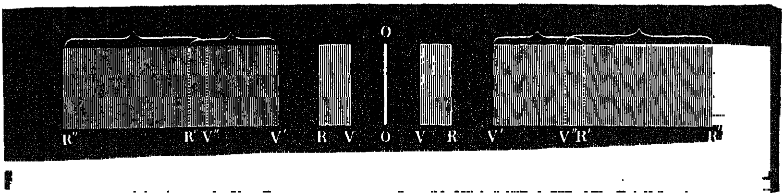


FIG. 11.

In the triangle BDE—

the ratio $\frac{DE}{BD} = \cos BDE = \sin\theta$, where θ is the angle X_4DM_4, or, as it is called, the angle of diffraction.

It follows, therefore, that—

$$DE = \sin\theta \times BD.$$

Now BD is the width of an aperture of the grating *plus* the adjacent dark space; it is called the grating space, and is usually denoted by the letter b. We have thus obtained the result that the wave-length of a ray of light is equal to the product of the grating space into the sine of the angle of diffraction; the wave-length of an unknown ray may be found, therefore, by measuring the angle of diffraction obtained with a grating, and by multiplying the sine of this angle by the width of the grating space.

This, however, is only true for the two spectra of the first order, and if it is to hold good for all the orders it must have a more general form. If the wave-length is denoted by λ we may write—

$$n\lambda = b \sin\theta_n,$$

when n stands for the number of the order and θ_n for the angle of diffraction for the nth order.

This development of the theory of diffraction, and its application as a practical means of measuring the wave-length of light, Fraunhofer published in 1821 in a paper he read before the Munich Academy of Sciences. He made his first gratings by winding silver wire round a brass frame, taking great care, of course, to preserve the grating spaces thus produced quite regular for the whole distance. The wires he used in different cases varied in thickness from 0·04 mm. to 0·6 mm., and the grating spaces varied correspondingly from 0·6866 mm., to 0·0528 mm. Fraunhofer made measurements of the black lines in the solar spectrum which he had labelled B, C, D, E, F, G, and H, and the ten values he obtained of the wave-length of the D line with ten different wire gratings were extraordinarily accurate, if we consider that, owing to the large size of his grating spaces, the angles of diffraction were of the order of one minute of arc. The actual values he obtained were as follows:—

0·0005891 mm	0·0005888 mm.
0·0005894 ,,	0·0005885 ,,
0·0005891 ,,	0·0005885 ,,
0·0005897 ,,	0·0005882 ,,
0·0005885 ,,	0·0005882 ,,

Soon after this Fraunhofer succeeded in making gratings by ruling equidistant and parallel straight lines on flat glass plates; he made two such instruments with grating spaces equal to 0·0033 mm. and 0·016 mm. respectively, and with these found the wave-length of the D line to be 0·0005886 mm. and 0·0005890 mm. The value of this constant as adopted at the present time is about 0·0005893 mm.

The importance of Fraunhofer's work cannot be over-estimated; on the one hand, by his investigation of the black lines of the solar spectrum he first showed the possibility of making accurate measurements of the relative dispersive powers of substances, from an ignorance of which Newton failed in making refracting telescopes; on the other hand, by his work on diffraction he founded a method of making absolute measurements of the wave-length of light.

The actual physical significance of the black lines in the spectrum of sunlight was, of course, unknown to Fraunhofer, and it was only by slow steps that any advance was made towards their explanation, which was discovered about thirty-five years later. It had long been known that when certain metallic salts were fed into a flame, such as that of a spirit-lamp, different colours were produced, and in 1822 Sir John Herschel observed that, if such flames were examined through a prism, the light was resolved into single rays, and that bright lines were visible on a dark ground, that is to say, discontinuous spectra were obtained. This fact was also known to Fraunhofer, who further noticed that the yellow spectrum line obtained from the light of the flame of a spirit lamp fed with common salt was identical in position with the D line of the solar spectrum; he also observed that the line in both these cases consists of a close pair of lines of equal intensity. It is difficult to decide as to who first made the discovery of the true connection between the bright spectrum

lines obtained from metallic salts in a spirit-flame and the Fraunhofer lines, but certainly in 1848 Foucault showed that, if the very powerful light from the electric arc were passed through a flame tinted yellow by a sodium salt, and then examined in a spectroscope, black lines appeared in the spectrum in the identical positions of the D lines. This important result was, however, apparently unnoticed until the whole matter was investigated and completely explained by Kirchhoff in 1859, who, in papers read before the Berlin Academy of Sciences, gave a mathematical deduction and experimental proof of the great law which is known under his name. This law stands as follows:—The relation between the powers of emission and the powers of absorption for rays of the same wave-length is constant for all bodies at the same temperature.

This law of Kirchhoff's thus expresses the following facts. First, a substance when excited by some means or other possesses a certain power of emission; it tends to emit definite rays, the wave-lengths of which depend upon the nature of the substance and upon the temperature. Second, the substance exerts a definite absorptive power, which is a maximum for the rays it tends to emit. Third, the ratio between this emissive and absorptive power is constant for all substances at the same temperature. We must imagine, therefore, that the particles of a substance when excited become endowed with the power of emitting energy which gives rise to waves in the ether, the lengths of these waves being a function of the chemical nature of the substance. The converse of this must also be true and the particles when excited must absorb the same waves when exposed to white light.

Attention may be drawn to an interesting and important result that follows from Kirchhoff's law. Since the ratio between the powers of absorption and emission is a constant, it is evident that the greater the opacity of a body the more complete its spectrum, and conversely, the greater the transparency of a body the less complete its spectrum. A lump of metal, for example, when heated to a high temperature must give a continuous spectrum, whilst, on the other hand, a transparent body cannot be made to incandesce. In order to obtain the true emission spectrum of a substance, namely, that characteristic of its component atoms, it must be dealt with in the state of gas.

Kirchhoff was enabled to form a theory of the constitution of the sun based on his knowledge of the origin of the black lines in the solar spectrum. He conceived the idea that the sun is surrounded by a layer of vapours of many substances, which act as filters, so to speak, of the pure white light arising from the incandescence of the interior body of the sun, and abstract therefrom those rays which correspond in their periods of vibration to those of the component molecules of the vapours. This layer is called the reversing layer, because Kirchhoff gave the name reversal to the process of absorption which gives black lines in the spectrum of a substance in place of the bright lines obtained in the emission spectrum. The Fraunhofer lines thus become of extreme importance inasmuch as they form a source of information as to the actual composition of the sun, the existence of an element in the sun being

proved by the coincidence of the lines of its emission spectrum with lines in the solar spectrum.

As a natural result of Kirchhoff's discovery a great impetus was given to spectroscopic work, and attention was at once turned to the examination and mapping of the emission spectra of terrestrial substances with the view both of putting these on record and of testing their presence or absence in the solar atmosphere. Bunsen and Kirchhoff stand foremost, with a long investigation into the spectra of many substances; they succeeded also in obtaining reversals of a number of the lines, and in establishing the presence of many elements in the sun. They drew maps of the spectra they observed, which for some time were used as standards of reference, but unfortunately all the results were expressed upon a purely arbitrary scale. The whole spectrum was divided up into a number of equal divisions, which were numbered, and the positions were noted which the observed lines bore as regards this scale. Kirchhoff also used a similar scale in his work on the spectrum of the sun, and thus the whole of his and Bunsen's individual and joint work was expressed in meaningless units.

Inasmuch as Bunsen and Kirchhoff had proved the existence of many terrestrial elements in the sun, it was a natural consequence that the solar spectrum itself should come to be the standard of reference. The sun possesses a further advantage as a standard, in that the Fraunhofer lines are very fine and sharply defined, so that very accurate determinations of their position are possible.[1] The measurement and mapping of the solar spectrum was carried out by A. J. Ångström, who, following Fraunhofer's lead, measured the wave-lengths of an extremely large number of the lines, and made a map of the spectrum, in which each line was placed according to its wave-length. This map was called by Ångström the Normal Solar Spectrum, and was published in 1868. This great research was carried out with the help of three gratings, which had been ruled on glass by Nobert, every care being taken to render the results as accurate as possible. The measurements covered the region between A and H, that is to say, all the visible spectrum, and the wave-lengths were expressed in ten-millionths of a millimetre, and carried to two places of decimals. This unit of length has been used ever since in wave-length determinations under the name of the Ångström unit.[2]

Now Ångström measured the three gratings by means of a dividing engine, and thus determined for himself the width of the grating space by comparison with the standard metre at Upsala. Unfortunately, however, the length of this standard metre had been wrongly determined by

[1] There are certain objections to the adoption of the solar spectrum as the standard of reference, which are discussed below, *vide* p. 204.

[2] The unit of length, the ten-millionth of a millimetre, equals 1×10^{-10} metre, and is often called, as suggested by Johnstone Stoney, a tenth-metre. Frequently, also, wave-lengths are expressed in thousandths of a millimetre (μ), or millionths of a millimetre ($\mu\mu$). The wave-length of the D_1 line, for example, may be expressed as follows:—

$$\lambda = 0{\cdot}589616\ \mu, \text{ or } 589{\cdot}616\ \mu\mu, \text{ or } 5896{\cdot}616 \text{ A.U. or t.m., or } 5{\cdot}89616 \times 10^{-5} \text{ cm.}$$

Tresca, who had compared it with the one at Paris on behalf of Ångström, with the result that all the wave-length measurements were a little too small. The actual length of the Upsala metre was afterwards found by Lindhagen to be 999·94 mm. instead of 999·81 mm., which was the value used by Ångström.

Ångström, on discovering the error, deputed his pupil Thalén to correct all the measurements, he himself being too old—indeed, he died before the corrections were finished. In addition to the complete re-calculation of Ångström's values, Thalén extended the work by determining the wave-lengths of the spark spectra of all the metals then known (44) by means of a prism spectroscope, directly referring the values to Ångström's normal map.

The publication of Ångström's map marks a definite stage in the development of spectroscopy; for the first time a standard of reference, placed upon a physical basis, was put upon record. The determination of wave-lengths of lines in unknown spectra was now made possible by a direct comparison between the unknown spectrum and that of the sun, and the calculation of the unknown wave-lengths by a simple process of interpolation between those of the lines in Ångström's map. An additional most important consequence was that the results of different experimenters were referred to the same standard and brought into line, so that they could be collated and compared amongst themselves.

CHAPTER II.

HISTORICAL—*continued*.

In the last chapter none of the work was taken into consideration which has been carried out by various experimenters upon the extreme ends of the spectrum. As is well known at the present time, the visible spectrum is but a minute fraction of the whole which extends in both directions far beyond the limits capable of detection by the eye. Recent work has established the existence of waves in the ether, the length of which lies between many hundred metres and one ten thousand millionth of a millimetre. The science of spectroscopy, however, does not embrace the study of the whole of these waves, the longer waves lying in the domain of wireless telegraphy. Spectroscopy deals with the phenomena of radiant energy associated with atoms and molecules which act as the absorbers or emitters of that energy, phenomena which would seem to be closely associated with the chemistry of substances. On the other hand, it is possible to picture elastic vibrations of matter giving rise to very long wave radiations. Such radiations, however, lie outside the confines of spectroscopy and it is not impossible that the waves employed in wireless telegraphy are of this type.

By various means emission spectra have been observed to as far as the wave-length 324μ, or 3,240,000 Ångström units, but by absorption spectrum methods the limit has been pushed to about 400μ. By indirect methods, which will be discussed under absorption spectra, it has been proved that substances can absorb and radiate energy of wave-lengths as great as 3000μ or 3 mm., these waves being undoubtedly connected with those shorter waves which are characteristic of atoms and molecules.

Since these waves are the longest yet proved to be specifically characteristic of atoms and molecules it would seem that the upper limit to the spectrum lies at or near this wave-length.

In the opposite direction the emission spectra of some elements have been observed to the wave-length of about 150 Ångström units, and, therefore, it might perhaps be considered that this marks the boundary of spectroscopy. On the other hand, modern work in the field of X-rays has clearly established the fact that these radiations are specifically characteristic of elementary atoms and therefore they must be included within our definition of spectroscopy. The X-rays possess wave-lengths of about 10 A.U. to 0·1 A.U. and therefore it may be said that the present limit of the spectrum lies at or about 0·1 A.U.

It must not be forgotten that there exist radiations of still smaller wave-length, the γ-rays associated with radioactive phenomena, their wave-length being believed to lie between 0·01 A.U. and 0·001 A.U.

The visible spectrum extends from about 7600 A.U. to about 3900 A.U. (individual observers vary in their powers of visual sensation) and thus this region forms a very minute fraction, less than one hundred thousandth, of the whole spectrum.

The history of the discovery and the early investigation of the invisible regions is extremely interesting. It is noteworthy that a fact pointed out by the chemist Scheele in 1777 was the origin of the discovery of the invisible portion beyond the violet. He knew that the salt silver chloride possesses the property of changing from white to purple when exposed to sunlight, and on investigating the effect of the different colours of the spectrum he found that the greatest effect was produced when the silver chloride was exposed to the extreme violet end. Scheele found in this way that the activity of the rays of the spectrum increased towards the violet end.

The actual discoverer of an invisible spectrum was Sir William Herschel in 1800, who was making some experiments upon the different colours of the spectrum with a view of finding that which had the least heating power, as he wished to obtain the most suitable colour for sun glasses to use with his telescope. Herschel caused a beam of sunlight to pass through a prism, and then tested the heating power of each colour upon the bulb of a delicate thermometer; he found that the maximum effect was obtained in the region beyond the visible limit of the red.

In 1840 Sir John Herschel continued the investigation of the subject, and succeeded in proving the fact that the spectrum actually extended beyond the visible limit, and that the Fraunhofer lines were continued into this region. His method of proving this was one of great ingenuity. He painted a sheet of paper with gum and lampblack so as to make it readily absorptive of heat; this paper was then dipped into alcohol and exposed to the sun's spectrum. Had the invisible portion been quite continuous, the alcohol, being so volatile a liquid, would have entirely evaporated, leaving a dry strip where the invisible spectrum had been projected on to the paper. This, however, Herschel found not to be the case, for only partial drying took place, and three or four damp patches were left which marked the presence of groups of absorption lines in the invisible region. The investigation was taken up more fully soon afterwards by many experimenters, and the spectrum was proved to extend far beyond the limit of visibility in the red, and to contain many of the Fraunhofer absorption lines. This portion of the invisible spectrum, which is called the infra-red, consists of the rays of longer wave-lengths which evidence themselves as radiant heat, and, therefore, may be readily examined by means of a thermopile, and most of the investigations have been carried out with the help of such apparatus. These apparatus improved in delicacy as time went on, and the emission spectra were found to extend a very great distance in this direction.

Amongst other important work upon this part of the spectrum may be mentioned that of Langley in America, who made use of an exceedingly delicate electrical resistance thermometer, which he called a bolometer, and made investigations chiefly into the infra-red portion of the solar spectrum. It is interesting to note that photographic plates have been made which are sensitive to these heat rays, and Abney and others have succeeded in obtaining photographic records which extend a considerable distance into this region. During more recent years we have been indebted to Paschen and more especially to Rubens for most important and pioneer investigations in the infra-red. To Rubens we are indebted for the opening up of the long wave region to as far as the wave-length 400μ. This work has been carried out with prisms and lenses and with gratings and mirrors, the recording instruments being the bolometer, thermopile, radiometer, and radiomicrometer. A full account of this work will be given in Chapter VIII. Equally important, too, are the indirect methods of measuring the very long wave infra-red radiations characteristic of atoms and molecules. These methods were initiated about eleven years ago by Bjerrum and, since these are more closely connected with the absorption than the emission of energy, they will be discussed in Volume II., Chapters VI. and VII.

As was natural after Sir William Herschel's discovery of the infra-red spectrum, it was soon asked whether or no there existed a similar extension beyond the violet, and in 1803 Inglefield drew attention to Scheele's observations on silver chloride, and thought in consequence that such an extension did exist. The first actual demonstration, however, of there being an ultra-violet region was made by Ritter and by Wollaston, who showed that the blackening of the silver chloride took place quite readily in the regions of the spectrum beyond the visible limit in the violet. In 1842 E. Becquerel succeeded in proving the presence of the Fraunhofer absorption lines in this region of the solar spectrum, by projecting it on to strips of paper which were coated with silver chloride; in this way he photographed it, and detected the presence of a long ultra-violet region which contained many Fraunhofer lines. These he labelled, following Fraunhofer's lead, with the letters L to P, which meant the extension of the spectrum to the limit of about $\lambda = 3400$ Ångström units. This ultra-violet region can best be examined by photographic methods, because the rays of shorter wave-length which compose it happen to be active towards silver salts, and, therefore, investigations in this direction are more easily carried out than those in the infra-red. Glass, however, readily absorbs these rays when they are of shorter wave-length than about 3300 Ångström units, and therefore more transparent substances must be made use of for lenses and prisms. Stokes has shown that quartz and Iceland spar are very transparent to these rays of short wave-length, quartz being the better of the two, because Iceland spar absorbs all waves of lengths shorter than 2150 units. With an apparatus fitted with quartz lenses and prisms it is possible to reach as far as $\lambda = 1850$ A.U., provided that the rays have not far to travel through air, since it has been found that oxygen begins to exert a

strong absorptive power towards light of shorter wave-length than 2000 A.U In addition to this, the photographic plate begins to fail beyond 2100 A.U. owing to the fact that gelatine is a powerful absorber of these rays of short wave-length, with the result that the silver bromide is protected from their influence.

In order, therefore, to investigate the region beyond 2000 A.U. it is necessary to employ special apparatus. The pioneer in this field was Schumann who constructed a vacuum spectrograph, fitted with lenses and prism made of fluorite, and employed photographic plates with little or no gelatine. With this apparatus he was able to photograph emission spectra to as far as 1200 A.U. This work was continued and extended by Lyman, McLellan, and by Millikan, a very notable improvement being the substitution of a grating for the fluorite lenses and prism. With such apparatus it is an easy matter to reach the wave-length of 600 A.U., and indeed Millikan has succeeded in photographing emission spectra to as far as 144 A.U. This work will be described in Chapter VIII., whilst the technique of X-ray spectroscopy will be dealt with in Volume II., Chapter II.

The extension of Ångström's Normal Map of the solar spectrum and the mapping of the ultra-violet region was carried out by Cornu, and was published in part in 1874, and the remainder in 1880. Cornu, of course, used photographic methods, and obtained his spectrum with gratings ruled by Nobert, similar to those used by Ångström.

The stage in the development of spectroscopy reached at the time of the appearance of Ångström's normal solar spectrum marks its birth as an exact physical science. More and more experimenters entered this field of research, and advances were made in every direction. It is, however, only possible in this short introduction to discuss the work directly leading to the establishment of the standards of reference. With the growth of the science during the next quarter of a century we cannot deal; we must leave it here and take up the thread again at the time when Ångström's map was superseded. This was first done by Rowland, who published a complete normal photographic map of the solar spectrum, based upon a new invention he made in connection with the ruling and mounting of gratings. This map was about 20 metres long, and had a scale of wave-lengths attached, the maximum error in any part being estimated to be under 0·01 of an Ångström unit. The measurements were entirely based upon a new determination of the absolute wave-lengths of one of the D lines which had been carried out previously by Bell and others. This value is rather greater than that determined by Ångström and corrected by Thalén, and therefore the wave-lengths on Rowland's scale are generally greater than on that of Ångström. The difference, however, was not constant, and varied from about 0·5 to about 1·8 A.U. in different parts of the spectrum. By common consent, in view of the probable accuracy of Rowland's method and work, his scale was universally adopted as the standard of reference.

In the first chapter the theory of gratings was discussed only as far as it had been carried by Fraunhofer; the simplest case was then given,

namely, that of a transmission grating receiving light normal to its ruled surface. In this simple case it was shown that if λ stands for wave-length, b for the grating space, and θ_n for the angle of diffraction corresponding to the order of spectrum n, the relation holds good that—

$$n\lambda = b \sin \theta_n.$$

Now, a great advance in ruling gratings was made by Rutherford of New York, who first ruled glass gratings, and by afterwards silvering them obtained reflection gratings, *i.e.* gratings which give their spectra by reflected light. He finally succeeded in producing very fine reflection gratings by ruling a polished plane metal surface, which in reality presents an easier surface to rule than glass, as it is not so hard, and therefore the ruling diamond is not so much worn. The theory of the production of the spectra with a reflecting grating follows directly from that already given in Chapter I., the source of light acting as if it came from behind the grating and made some finite angle with the normal. The latter case, that of a transmission grating receiving an oblique beam of light, is shown in Fig. 12.

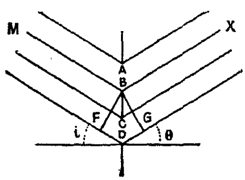


FIG. 12.

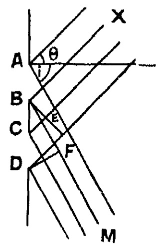


FIG. 13.

As before, in Fig. 10 (p. 16), only two grating apertures are drawn, AB and CD, these being sufficient for the present purpose. A parallel beam of light falls obliquely on to the grating from M, making the angle of incidence i with the normal; a great portion of the light passes directly through the apertures, whilst a portion is diffracted in the direction of X, these rays making an angle of diffraction θ with the normal. If now the perpendiculars BF and BG be drawn, it will be seen that the difference in path travelled by the corresponding rays in each pencil, or the retardation as it is called, is given by the sum of the lengths FD and DG, and therefore when these two lengths together are equal to some number of whole wave-lengths no interference takes place, and a bright image is produced when the diffracted rays are brought to a focus. Now, FD can be shown to be equal to BD sin i, and DG to be equal to BD sin θ,

and therefore $\lambda = \mathrm{BD}(\sin i + \sin \theta)$,
or more generally $n\lambda = b(\sin i + \sin \theta_n)$.

In all cases when the light falls obliquely on the grating a certain amount of retardation is dependent on the angle of incidence as well as on the angle of diffraction.

Exactly parallel is the case of a reflecting grating, as can be seen from Fig. 13.

A beam of light falls obliquely on the grating, making an angle of incidence i with the normal, and a portion is diffracted towards X, the angle of diffraction being θ. The perpendiculars BE and DF are drawn, and as before the lengths DE and BF represent the retardations. Now, the ray MB is retarded on the corresponding ray MD by an amount equal to the length BF, but, on the other hand, the ray DX is retarded on the ray BX by an amount equal to DE, and therefore the total retardation is equal to BF − DE;

but $\qquad \text{BF} = b \sin i,$

and $\qquad \text{DE} = b \sin \theta;$

therefore the total retardation $= b(\sin i - \sin \theta)$.

When this value is equal to one or more whole wave-lengths a bright image is seen, and therefore we have the general equation—

$$n\lambda = b(\sin i - \sin \theta_n).$$

If the diffracted rays are on the other side of the normal, that is to say, the same side as the incident rays, then clearly the two retardations are additive, and thus we have the general equation for all the spectra—

$$n\lambda = b(\sin i \pm \sin \theta_n),$$

the positive or negative sign being used when the incident and diffracted rays are on the same or opposite sides of the normal respectively.

Rowland was led to his work on gratings by finding in his search for a source of monochromatic illumination that a good grating was a necessity. He at once recognized that the key to a good grating lies in a perfect screw, and hence he set to work to make one. This he succeeded in doing, and was able thereby to make a dividing engine for ruling gratings far more accurately than had ever been done before.

The screw is first of all cut with the desired pitch and rather longer than is required, a nut several inches long is also cut, with a female screw of the same pitch so as accurately to fit the male screw. This nut is made in four sections, which are clamped together on the male screw. This clamped nut is then worked backwards and forwards along the whole length of the male screw for a very long time, and in this way all the errors are averaged down until they are evenly distributed over the whole length. The nut, of course, requires continually to be tightened during the process to take up the wear, and the temperature must be carefully kept constant. In this way extremely accurate screws can be cut, and indeed all screws for fine micrometers and such apparatus are now made by this method. When he had obtained a screw sufficiently accurate for his purpose, Rowland constructed a grating ruling machine, and succeeded in making gratings far finer than any that had previously been prepared. He was able to produce gratings with a ruling of 100,000 lines to the inch, though the closeness of the ruling renders such gratings too troublesome to prepare for ordinary purposes.

The principle involved in the ruling of a grating is the drawing of a fine diamond edge across the polished surface of glass or speculum metal in one direction only. The ruling carriage carrying the diamond point is moved between each stroke a definite amount in a direction at right angles to the stroke. This movement is effected by means of a micrometer screw, and of course it will be evident that the degree of perfection of the grating will depend upon the accuracy of this screw. The machine is driven by clockwork, it being so arranged that when once started a whole grating can be ruled without any attention. This is of great importance, because it is obvious that the process of ruling a whole grating, which in the case of the large size takes six days and nights, must be carried out at a constant temperature so as to guard against any expansion or contraction of the surface that is being ruled. One of the difficulties which frequently occurs is the wearing out of the diamond point, since if any essential change takes place in the shape of the diamond edge the grating will be ruined. It will be readily understood that the successful ruling of a grating is a very delicate operation. It has now been found possible to produce replica gratings either by photography or by making celluloid casts from a ruled grating. For an account of these see p. 182.

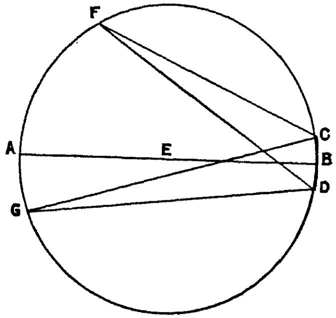


FIG. 14.

In 1881 Rowland conceived the idea of ruling gratings on a spherical mirror of speculum metal. In the previous examples in dealing with the spectra produced by gratings the use of lenses has been assumed for bringing the diffracted rays to a focus, but with a concave grating these are dispensed with, because the grating itself, being ruled on a spherical mirror, focuses the rays and produces the spectra. The mathematical properties of the concave grating Rowland has completely investigated, and the instrument has proved to be one of the greatest inventions ever made in spectroscopy. The methods of mounting the instrument and of working with it will be fully given in Chapter VII., but to a certain degree they must be described at this point in order to explain by what means Rowland arrived at the determinations of his solar standard.

The most important property of this grating, shown by Rowland, is that if the source of light, *i.e.* the slit, and the grating, be placed on the circumference of the circle which has the radius of curvature of the grating as diameter, the spectra will always be brought to a focus on this circle. For example, let AB in Fig. 14 be the radius of curvature of the grating CD; the circle AFBG is drawn with radius $\frac{AB}{2}$, that is, with E as centre. Then if the slit be placed on the circumference of

this circle, for example at F, the spectra will be formed round the circumference, so that if an eyepiece be placed at G the spectra will be seen in perfect focus, and may be examined by moving the eyepiece round the circle.

Furthermore, Rowland showed that great advantages accrue if observations are made on the spectrum normal to the grating. In the equation deduced on p. 27, we have

$$\lambda = b(\sin i \pm \sin \theta),$$

and therefore when the spectrum is observed directly normal to the grating—

$$\lambda = b \sin i, \text{ because } \theta = 0.$$

If now the eyepiece be moved a very small distance to one side of the normal, then—

$$\lambda + C = b \sin i \pm b \sin \theta,$$

where C is the small change in wave-length observed, and θ is the angular distance through which the eyepiece has been moved. It follows that C is proportional to $b \sin \theta$, and therefore to θ itself, because b is a constant and the sines of small angles are proportional to the angles themselves. But the angle θ is proportional to the linear distance through which the eyepiece was moved, and therefore it follows that the linear distance through which the eyepiece moves is proportional to the change in wave-length observed, or, in other words, for small distances on each side of the normal the spectrum is itself normal. This fact, which is true, of course, for every grating, both flat and concave, is most important, resulting as it does in the observation of truly normal spectra, for in the mounting adopted by Rowland for his concave grating the eyepiece of photographic plate is automatically kept in a position normal to the grating.

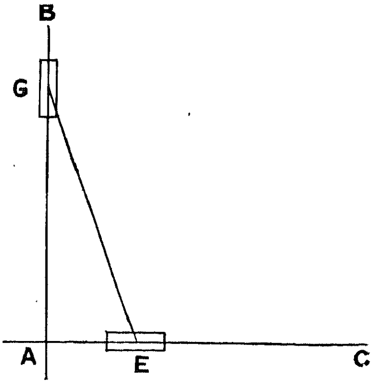


FIG. 15.

AB and AC in Fig. 15 are two girders rigidly fastened to supports, and they carry rails which are accurately adjusted at right angles to one another. On each of these rails runs a carriage, G and E, these two carriages being joined by a beam, GE. This beam is fitted to the carriage in each case by a vertical bearing so as to allow the carriages to move along their rails. The slit is then set up over the intersection of the rails at A, the grating at G, and the eyepiece or photographic plate at E. Under these circumstances it is evident that wherever the

grating and eyepiece may be placed, the circle having GE as diameter always passes through the three points G, A, and E.

Furthermore, in order that normal spectra may be always observed, the grating is placed normal to the direction GE, and therefore, by construction, E is made to coincide with the centre of curvature of the grating. When a photographic plate is employed in place of the eyepiece at E, it is necessary that it be bent to fit the circular focal curve, when it becomes possible to photograph a considerable portion of the spectrum normal.

Rowland pointed out that a second very valuable property also results from the above mounting of the grating, and on this he based his method of relative wave-length determination. In Rowland's special case, as above, the equation of wave-length is simplified to—

$$n\lambda = b \sin i,$$

when observations are made normal to the grating.

It follows, therefore, that for one particular position of the slit—

$$\begin{aligned} \lambda' &= b \sin i \text{ in the first order,} \\ 2\lambda'' &= b \sin i \quad ,, \quad \text{second order,} \\ 3\lambda'' &= b \sin i \quad ,, \quad \text{third order, and so on,} \end{aligned}$$

where λ', λ'', λ''', etc., are the wave-lengths in the first, second, and third, etc., orders.

We have therefore—

$$\lambda' = 2\lambda'' = 3\lambda''', \text{ etc.,}$$

and thus, at any position of the slit, the various orders of spectra are superposed, and the wave-lengths of each are inversely proportional to the number of the order. For example, on a wave-length of 9000 Ångström units in the first order are superposed 4580 in the second order, and 3000 in the third, and 2·250 in the fourth; on a wave-length of 6000 in the third order are superposed 4500 in the fourth order, 3600 in the fifth, 3000 in the sixth, and so on.

These two properties, namely, the normality of the spectrum and the relation of the superposed orders, enabled Rowland to measure the wave-lengths of all the lines in the solar spectrum with great accuracy relatively to the wave-length of one line. This, as before-mentioned, was the D_1 line, the wave-length of which was adopted as 5896·156 as a mean of the best measurements. By measuring the lines in the various superposed orders in relation to the D_1 line, Rowland first determined the wave-lengths of fourteen lines in different parts of the spectrum with the greatest possible accuracy, and in a similar way from these lines he determined the wave-lengths of the principal lines throughout the spectrum. He then photographed the whole normal spectrum from end to end, and from his knowledge of the wave-lengths of all the principal lines he was able to rule the scale of wave-lengths on each plate, and then to enlarge each photograph and its scale

together. In this way a very large map of the whole spectrum was obtained, with the scale attached from which the wave-length of any line could be read with great ease. The beauty of the method seemed to lie in the fact that, though the wave-length of the D_1 line is the basis of the scale, yet the relative accuracy of the scale throughout is exceedingly great, far greater than ever possible with separate wave-length determinations.

Rowland was under the impression, owing to the accuracy of these measurements, that if at any time a more correct determination of the wave-length of the D_1 line were made it would only be necessary to multiply his numbers and all determinations referred to them by some small factor. As a matter of fact, as will be seen from the sequel, the accuracy of Rowland's work is not nearly so great as was at first supposed. His measurements contain a periodic error which of course precludes any correction of the whole by multiplying by a constant factor.

Bell's determination of the absolute wave-length of the D_1 line was undertaken with a view of making a standard for Rowland's work; he had access to more accurate and finer gratings than had been obtainable by previous workers, and it was thought that a more accurate value of this constant could be obtained. An account of the methods employed and the results were published in 1887 and 1888,[1] the first paper referring to measurements with two glass gratings, whilst the second is a much more extended discussion of these and some further measurements with two reflecting gratings, and contains a full account of the errors and methods adopted to eliminate them. These errors arise from the inevitable small imperfections occurring in the ruling of the gratings, errors which are by far the greatest to be met with in the investigations. Bell points out that there are five more or less different methods of making the measurements, depending on the position of the grating in relation to the collimating and observing telescopes. The wave-length equation may be written in the form—

$$n\lambda = b\{\sin i + \sin (\phi - i)\}$$

if i be the angle of incidence, and ϕ the angle of deviation; then if i be made equal to zero the equation will be simplified to—

$$n\lambda = b \sin \phi,$$

which applies to the first two methods, in which the grating is placed normal to the collimator and observing telescopes respectively.

The third method is the one adopted by Ångström, in which the grating is set nearly perpendicularly to the collimator, and the angle of incidence i formed is measured and kept in the formula.

The fourth method is the one of minimum deviation, which can be shown to take place when the angle of incidence is equal to half the

[1] *Phil. Mag.*, **23**, 265 (1887), and **25**, 255 and 360 (1888).

angle of deviation; in this case the wave-length can be found from the equation—

$$n\lambda = 2b \sin \frac{\phi}{2}.$$

The fifth method consists in clamping the collimator and telescope at some known angle with each other, and then rotating the grating. The equation $n\lambda = b\{\sin i + \sin(\phi - i)\}$ can be written in the form—

$$n\lambda = 2b \sin \frac{\phi}{2} \cos \left(i - \frac{\phi}{2}\right),$$

and therefore, if δ be the angle through which the grating is turned, and θ the angle between the collimator and telescope, we will have—

$$n\lambda = 2b \sin \delta \cos \frac{\theta}{2}.$$

The method of observation is to adjust the required line upon the cross-wire in the eyepiece, and then rotate the grating until the reflected image is brought upon the cross-wire.

In his own determinations Bell used the second method, with the grating normal to the observing telescope, in the case of two glass transmission gratings, and the fifth with two reflecting gratings ruled on speculum metal. The first two methods are, indeed, the most satisfactory for transmission gratings, because only one angle has to be measured, whilst the fifth method was adopted for the speculum metal gratings owing to the great weight of the telescopes employed, which were of 16·4 cms. aperture and 2·5 metres focal length. As regards the gratings, they differed very considerably amongst themselves in the matter of size and grating-space; the first was 30 mm. long, with 12,100 lines, and the second was almost the same length, with 8600 lines; these were ruled on different parts of the screw of the dividing engine. The third was 4 inches long, and contained 29,000 lines, and the fourth was the same length, and contained 40,000 lines, being ruled with another dividing engine. The actual readings of the angles were made within one second of arc in every case, and a mean of a very great many was adopted as a final result, the probable error being extremely small. The measurements with the first two gratings were made with the D_1 line in the third and fourth orders respectively, while, with the second apparatus and the third and fourth gratings, other lines had to be observed owing to the limits imposed by the fixed telescopes. With grating No. 3, the line at $\lambda = 5133·95$ was measured in the eighth order, and with the fourth grating the line at $\lambda = 5914·32$ was measured in the fifth order. From these the wave-length of D_1 could be calculated from Rowland's table of wave-lengths.

By far the most important portion of the work was the determination of the grating-spaces in each grating, and herein lay the most fruitful source of errors. The actual determination of this length was made by comparison with standards of length, which were themselves compared

with the international standards with the greatest possible care. It was, however, not found possible simply to measure the length of the ruled space, and divide this by the number of lines ruled, in order to determine the grating-space, owing to the inevitable inaccuracies which occur to a greater or less extent in every grating. Bell points out in his paper that the grating space is never regular throughout the whole extent of the ruled surface, and the variations may be classed as regular and irregular. In the first class are put those which are periodic or linear, which produce respectively "ghosts"—that is to say, false images, and differences in focus on opposite sides of the normal. These are not so serious as the variations of the second class, which include the displacement, omission, or exaggeration of a line or lines, and more especially a more or less sudden change in the grating-space producing a section of the grating having a grating-space peculiar to itself. Bell describes the testing of a grating in the following words:—"Place a rather bad grating on the spectrometer, and, setting the cross-hairs carefully on a prominent line, gradually cover the grating with a bit of paper, slowly moving it along from end to end. In very few cases will the line stay upon the cross-hairs. A typical succession of changes in the spectrum is as follows:—Perhaps no change is observed until two-thirds of the grating has been covered. Then a faint shading appears on one side of the line, grows stronger as more and more of the grating is covered, and finally is terminated by a faint line. Then this line grows stronger till the original line appears double, and finally disappears, leaving the displaced line due to the abnormal grating-space." Although the above is perhaps exceptional, still minute displacements can be seen even with very good gratings. It becomes necessary, therefore, always to examine the grating for the existence and position of any abnormal portion, an investigation which is somewhat simplified by the fact that for the most part abnormal spacing occurs at the end of the ruled surface, generally at the end where the ruling was begun, because the dividing engine after starting requires some time to settle down to a uniform state. Bell recommends the calibration of the entire grating—that is to say, the direct measurement of n grating-spaces taken successively along the whole of the ruled surface; he carried out this process for all of the four gratings, and found in each some abnormal portion. The values obtained from these observations were combined in each case, and corrections applied to the wave-length as first obtained; evidently these at the best can only be approximate, for on the one hand a minute examination of a grating spectroscopically is impossible, since a small section of ruled surface does not give measurable spectra, and on the other hand, while the calibration values are very accurate, it is impossible to decide exactly how any variations in the grating-space are integrated in the spectrum measured.

A further possible source of error lay in the temperature of the grating, on which of course depends the value of the grating-space. This could easily enough be corrected for when the temperature was known, since the coefficients of expansion have been very accurately

determined. The determination of the temperature with the metal gratings was easily made owing to their being such good conductors of heat; in the case of glass gratings, on the other hand, great care had to be exercised in order to keep the temperature constant, because, though glass has such a small coefficient of expansion, yet, being so bad a conductor, it may give rise to serious errors due to straining and bending from unequal heating.

The corrected results which Bell obtained with the four gratings were as follows:—

Grating I.,	wave-length D_1	5896·18
„ II.	„ „	5896·23
„ III.	„ „	5896·15
„ IV.	„ „	5896·17

of which the mean value is 5896·18 in the air at 20° and 760 mm. pressure, and 5897·90 *in vacuo*. These numbers were, however, subjected to a further correction, and were finally given as 5896·20 in air, and 5897·92 *in vacuo*, while Ångström's value as corrected by Thalén was 5895·81. Important determinations have also been made of this constant by Müller and Kempf, Peirce, and Kurlbaum. Müller and Kempf made use of four gratings ruled on glass by Wanschaff, and obtained the following somewhat widely differing values at 15° C.:—

	λ
Grating-space, 2151	589·646
„ „ 5001	5896·14
„ „ 8001	5896·33
„ „ 8001	5895·97

The mean of these is 5896·22, which becomes 5896·25 at 20°. The value Peirce obtained with Rutherfurd's gratings was 5896·27, which, as a result of the calibration of his grating by Bell, was reduced to 5896·20.

Kurlbaum, in his investigation, employed two gratings, one by Rutherfurd and the other by Rowland, the first having 29,521 lines in a space of 43·4 mm., and the other 23,701 in 41·7 mm. The length of the ruled spaces in these gratings rendered the measurement of the grating-space a matter of considerable difficulty, owing to their not being a definite fraction of a metre. The values he obtained were 5895·84 and 5895·96 respectively, and the mean of these is equal to 5895·90 units. These determinations Rowland combined together, weighting them according to the value of the result as follows:—

Weight.	Observer.	D_1.
1	Ångström, as corrected by Thalén	5895·81
2	Müller and Kempf	5896·25
2	Kurlbaum	5895·90
5	Peirce	5896·20
10	Bell	5896·20
	Mean	5896·156

This final value Rowland adopted as the standard of his wave-length determinations, and hence it is the standard of all the measurements with prism or grating apparatus based on his standard.

It is unfortunate in view of the extreme care which Rowland took in preparing his table of standard wave-lengths that his main contention was proved to be unsound, namely, that the values were relatively correct and that a new value for the wave-length of the D_1 line would merely necessitate a proportional change in all his measurements.

In 1894, Michelson by a new method succeeded in determining the absolute wave-lengths of three lines in the spectrum of cadmium in relation to the standard metre at Paris. The method employed was the determination by interference methods of the number of waves of the three spectrum lines contained in 1 metre. The details of the interference apparatus will be found in Volume II., Chapter I., and cannot be dealt with here; suffice it to say that the method is free from all the inherent errors of grating measurements, and the values of the three wave-lengths as given by Michelson were generally accepted as being absolutely accurate. The actual values were—

Red line	1 metre	$= 1553163{\cdot}5 \times \lambda \therefore \lambda = 6438{\cdot}4722$	tenth metres
Green	,, ,,	$= 1900249{\cdot}7 \times \lambda \therefore \lambda = 5085{\cdot}8240$	,, ,,
Blue	,, ,,	$= 2083372{\cdot}1 \times \lambda \therefore \lambda = 4799{\cdot}9107$	,, ,,

These values are considerably below those obtained from Rowland's tables, which are $\lambda = 6438{\cdot}680$, $5086{\cdot}001$, and $4800{\cdot}097$ respectively. Soon afterwards Fabry and Perot measured a number of lines in the spectra of certain metals and of the sun by interference methods, directly comparing them with Michelson's values for the cadmium lines. It was then found that the difference between the wave-lengths measured by interference methods and those on Rowland's map was not proportional to the wave-length. Clearly, therefore, either Rowland's relative values or the interference values are wrong. The discrepancy was explained by Kayser, who proved conclusively that the coincidence between the orders of spectra with gratings is not to be depended upon; for this and some other reasons he showed that Rowland's values are by no means good enough for our present needs—the error in them is far greater than the experimental error in accurate work at the present time.

There is no doubt, therefore, that grating measurements must give place to interference measurements, and during the last few years the new standard has been set up.

Before dealing with the details of the establishment of the new standards of wave-length, the question may be asked as to why the D_1 line of sodium has given place to the cadmium lines as primary standard. The answer to this question is to be found in the greater purity of the cadmium radiations. It is obvious, if the wave-length of a spectrum "line" is to be determined with sufficient accuracy for it to be adopted as an international standard for all quantitative spectroscopic measurements, that the radiations to which that "line" is due

must be as homogeneous as possible. As will be described in detail in Volume II., Michelson investigated and analysed the radiations comprised within the apparently single lines exhibited by many elements. He found that many "lines" are in reality very complex, consisting frequently of one principal line, together with many satellites grouped closely on either side of it. Such lines are useless for the purpose of fundamental standards of wave-length and it may be said at once that Michelson found the cadmium red line to be the purest and the most monochromatic of all those which he examined. As will be seen below, the wave-length of this line has now been finally adopted as the fundamental standard.

As the result of Michelson's and of Fabry and Perot's work the International Union for Co-operation in Solar Research was formed and this body undertook the problem of setting up the new standard. A first meeting was held at St. Louis in 1904 and the second meeting took place at Oxford in 1905. At the latter meeting it was decided that—

1. The wave-length of a suitable spectroscopic line shall be taken as the primary standard of wave-length. The number which defines the wave-length of this line shall be fixed permanently, and all wave-lengths shall be measured in the unit thereby defined. This unit shall be called the Ångström.

2. Secondary standards shall be measured by interferometer methods in reference to this primary standard, and these secondary standards shall not be more than 50 units apart.

At Meudon in 1907 the International Union again met and finally adopted the cadmium red line as the primary standard, and it was agreed to designate the wave-length as—

$$6438{\cdot}4696 \text{ Ångströms}$$

in dry air at 15° and a pressure of 760 mm. of mercury, the radiation being given by a cadmium vacuum tube with electrodes. The Ångström is defined in this way and is equal to the old Ångström unit with an accuracy of about 1 in 10,000,000. The minute difference between the finally adopted value of the wave-length and that published by Michelson is due to a small correction introduced by Benoit in collaboration with Fabry and Perot.

The fourth meeting of the Union was held at Mount Wilson in 1910, when it was decided to adopt as secondary standards the means of the values of the wave-lengths of lines in the arc spectrum of iron found by three independent observers, provided of course that no decided discrepancy is to be found in any of the measurements. It was also agreed that tertiary standards should be determined by interpolation methods from the secondary standards. To carry out this type of measurement it was dec[illegible] should be taken with concave gratings of spectra [illegible] [illegible]lopted as secondary standards, and that the wave-lengths of other lines should be determined by linear interpolation between these standards. At a later date the adoption of plane gratings or prism spectrographs of high dispersion was approved for this

purpose. It was also agreed that the symbol for the new unit, the Ångström, should be I.A. so as to guard against any possible confusion with the old standards of Ångström and Rowland.

The fifth meeting of the Union was held in Bonn in 1913 and certain secondary standards were adopted; further, the conditions for the use of the iron arc in air for the determination of the tertiary standards were defined in order to secure the necessary accuracy. These need not here be specified.

The war interrupted the work of the Union and the next meeting was held at Rome in 1922, the programme having been taken over by the International Astronomical Union. At this meeting the report of the Standard Wave-length Committee was approved, and in the following tables (see pp. 38-40) are given all the secondary and tertiary standards in the spectrum of iron that have definitely been accepted by the International Union up to the present date.[1]

For convenience in working in the orange and red regions of the spectrum the following wave-lengths of neon lines have been recommended as secondary standards—

Neon lines.

7032·412	6506·528	6217·280	6029·998
6717·042	6382·991	6163·594	5975·534
6678·276	6334·428	6143·062	5944·834
6598·953	6304·789	6096·163	5881·896
6532·882	6266·495	6074·338	5852·488

It will be noted that the first table does not extend beyond 3370 A and consequently that no international standards have as yet been adopted of smaller wave-length than this. It will not be long before the gap is filled, for individual observations have already been recorded, but, since they have not been confirmed by two other independent observers, they have not as yet received the final seal of approval as international standards and therefore they will not be quoted here. (See p. 133.)

In this historical introduction to Spectroscopy I have restricted myself to the establishment of the standards of wave-lengths and therefore have not discussed any work which has not reached the greatest accuracy at any period of the development of the science. There can be no question but that a very great amount of work can be carried out in which the optimum of accuracy is entirely uncalled for. There have been published many tables of wave-lengths which possess an accuracy fully sufficient for much important work but it is impossible to quote these in detail. Such tables of wave-lengths are given in Kayser's *Handbuch der Spectroscopie*, Volumes VI. and VII.

[1] *Trans. International Astro. Union*, I., 41 (1922), Imperial College Bookstall, London.

Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.
6750·163	6750·165	4		5446·921	6	4903·325	4903·326	5
6678·004	6678·001	5	5434·527	5434·528	6	4878·225	4878·224	5
	6663·455	4		5429·701	6	4859·758	4859·759	5
	6609·125	4	5405·780	5405·780	6		4802·886	2
6592·928	6592·927	5		5397·134	6	4789·657	4789·656	3
	6575·029	3	5371·495	5371·495	7		4788·762	2
6546·252	6546·252	5		5341·028	5		4786·812	3
	6518·382	3		5332·903	2		4772·818	3
6494·993	6494·993	5		5328·537	4		4745·808	3
	6475·639	3	5324·196	5324·196	6		4741·535	3
	6462·738	4		5307·365	2	4736·786	4736·790	5
6430·859	6430·859	5	5302·315	5302·315	5		4733·598	3
	6421·362	4		5270·360	8		4710·288	3
6393·612	6393·612	5		5269·540	10	4707·288	4707·290	5
	6380·753	3	5266·569	5266·571	8	4691·417	4691·417	4
	6344·161	2		5250·652	3		4678·856	5
6335·341	6335·342	4		5242·496	3		4673·171	3
	6322·696	3	5232·957	5232·956	8		4667·461	4
6318·028	6318·028	4		5227·193	8		4654·504	4
	6297·803	3		5216·280	5	4647·439	4647·439	4
6265·145	6265·145	3		5202·340	5			
	6254·267	3		5198·715	4		4638·019	4
	6252·567	4	5192·363	5192·360	8		4632·918	3
6230·734	6230·734	5		5171·601	7		4630·128	3
	6219·290	3		5168·903	3			
	6200·323	2	5167·492	5167·493	8		4619·297	4
6191·568	6191·568	5		5166·288	3	4602·947	4602·946	4
	6173·344	2		5151·916	3		4602·008	2
	6165·368	2		5150·845	4	4592·658	4592·657	4
	6157·734	2		5127·365	3		4587·136	2
6137·701	6137·702	4		5123·725	4	4547·853	4547·854	3
	6136·624	4	5110·415	5110·415	4	4531·155	4531·155	5
	6127·915	2		5098·706	4		4528·622	7
6065·492	6065·492	4	5083·344	5083·343	4		4517·532	2
6027·059	6027·059	2		5051·639	4		4514·193	2
5763·013			5049·827	5049·827	5	4594·572	4494·571	5
5709·396				5041·760	4		4490·088	2
5658·836				5041·076	3		4489·745	3
5615·661			5012·073	5012·073	4		4476·024	7
5586·772			5001·881	5001·881	5	4466·556	4466·556	5
5569·633				4994·135	3		4461·657	4
5506·784	550 ·784	4	4966·104	4966·106	5		4459·124	5
	5501·470	4		4939·691	3		4454·386	3
5497·522	5497·522	4		4924·776	3		4447·724	5
5455·614	5455·615	6	4919·007	4919·008	8		4443·199	3

Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.
	4442·346	5		4175·642	4		3966·067	7
	4435·154	2		4170·908	2		3956·682	4
	4430·621	4		4156·805	4		3956·461	4
4427·314	4427·314	5		4154·504	4		3952·606	4
	4422·573	4	4147·676	4147·675	4		3948·780	4
	4415·128	8r		4143·873	7		3942·444	3
	4408·421	4		4143·421	5		3940·884	4
	4407·716	2		4137·003	3		3937·332	2
	4404·754	8r	4134·685	4134·684	5	3935·818	3935·817	4
	4390·956	3		4132·905	3		3932·631	3
	4387·899	2		4132·062	7		3930·300	7R
	4383·550	10R		4127·614	4		3927·923	6r
4375·934	4375·934	5		4122·523	2		3925·947	3
	4369·777	3		4121·808	2		3922·915	6R
	4367·583	2		4120·212	2		3920·261	6r
	4358·507	2	4118·552	4118·552	6		3917·186	5
4352·741	4352·740	4		4114·451	4		3910·848	2
	4351·552	2		4109·809	4	3907·937	3907·937	3
	4346·561	2		4107·495	5	3906·482	3906·483	5r
	4337·052	—		4100·743	2		3903·903	3
	4327·101	2		4098·185	3		3902·949	7r
	4325·766	9r		4095·977	3		3899·710	6r
4315·089	4315·090	5		4085·011	2		3895·659	5r
	4307·909	8r	4076·642	4076·638	5		3888·518	7
	4305·457	2		4074·792	3		3887·052	6r
	4298·043	2		4067·985	5		3886·285	7R
	4294·130	6		4067·277	3		3884·362	2
	4285·449	2		4066·981	4		3883·284	2
4282·408	4282·408	6		4062·448	4		3878·575	6R
	4271·766	8r		4045·818	8R		3878·022	6r
	4267·832	2		4044·616	2		3873·764	4
	4266·970	2		4031·966	2		3872·505	6r
	4250·792	8	4021·872	4021·872	5		3871·752	2
	4245·261	2		4014·536	4		3867·220	3
4233·615	4233·614	6		4009·718	5	3865·527	3865·527	6R
	4226·426	2		4005·248	7		3859·914	7R
	4219·367	5		3997·397	6		3856·373	6R
	4216·188	4		3990·380	1		3852·577	3
	4213·652	2		3986·177	3	3850·820	3850·821	5
	4203·988	3		3983·962	5		3849·970	5
	4202·033	7r		3981·776	3		3846·805	6R
4191·443	4191·444	6	3977·746	3977·746	5	3843·261	3843·260	5
	4184·897	4		3971·327	4		3841·052	6R
	4181·761	6		3969·262	7r		3840·440	6R
	4177·599	2		3967·424	4		3839·260	5

Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.	Secondary standards.	Tertiary standards.	Intensity.
	3834·226	7R		3732·400	6		3585·321	6r
	3833·313	4		3727·622	6R		3584·664	5
	3827·826	6R	3724·380	3724·380	6		3582·202	4
	3825·885	8R		3722·565	6R		3581·196	8R
	3824·445	6R		3719·936	8R		3576·761	4
	3821·182	6		3715·915	2		3565·382	6R
	3815·843	7R		3711·226	2		3558·519	5r
	3814·527	2		3707·050	3	3556·881	3556·881	6
	3808·732	2		3705·568	6R		3545·642	5
	3807·541	4		3704·464	5		3542·080	5
	3806·702	6		3702·034	1		3541·083	6
3805·346	3805·346	6		3695·054	3		3529·821	4
	3799·550	6r		3690·731	2		3521·265	5r
	3798·514	6r		3687·459	6R	3513·821	3513·821	5
	3797·518	5		3684·112	5		3506·501	5
	3795·005	6r		3679·916	5r		3497·845	5r
	3794·342	3	3677·629	3677·629	6		3497·110	4
	3790·096	4	3676·313	3676·313	6		3495·291	4
	3787·884	6R		3669·524	6		3489·673	4
	3786·680	3		3659·520	5	3485·345	3485·343	6
	3785·950	5		3651·470	6		3476·707	5r
	3781·190	1		3649·509	6		3465·864	6R
	3776·457	2		3647·845	6R		3458·306	3
	3774·827	2		3645·825	4		3450·332	6
	3767·195	6R	3640·392	3640·392	6		3447·282	6
	3765·544	6		3638·300	6	3445·154	3445·153	4
	3763·791	6R		3632·041	6		3427·122	6
	3760·053	5		3631·465	6R		3424·289	6
	3758·236	7R		3630·352	3		3418·511	5
	3756·942	3		3625·149	5		3417·845	6
3753·615	3753·615	6		3623·188	5		3413·136	7
	3749·488	8R		3621·464	6		3407·463	7
	3748·265	6R		3618·770	6R		3402·262	4
	3745·903	5r		3617·789	6		3401·523	4
	3745·564	7R		3608 862	6R	3399·337	3399·337	6
	3742·623	1	3606·682	3606·682	5		3396·981	3
	3738·309	4		3603·207	5		3392·657	5
	3737·134	7R		3594·634	5		3380·115	5
	3734·868	9R		3589·108	4		3379·023	4
	3733·320	6R		3586·115	5	3370·789	3370·788	6

The letter R signifies that the line is reversed, and r that it is shaded or diffuse on the red side.

It is frequently necessary in spectroscopic work to make use of the frequencies of spectrum lines, and references will often be found in the literature to their wave numbers. By the wave number is meant the number of waves in one centimetre, whilst the frequency means the number of oscillations per second. The wave number is therefore given by

$$\frac{10^8}{\lambda \text{ in Ångströms}},$$

whilst the frequency is given by the wave number divided into the velocity of light, that is to say

$$\frac{3 \times 10^{10}}{\lambda \text{ in cms.}}.$$

Both of these refer to vacuum and therefore all wave-lengths must first be reduced to vacuum before the wave numbers or frequencies can be calculated. The wave-length in vacuo is given by the product of the wave-length in air into the index of the refraction of air for that wave-length. This is a lengthy procedure and it is very much more convenient to add a correction to the wave-length. We have

$$\lambda_{\text{vac.}} = \lambda_{\text{air}} \times n$$

and hence

$$\begin{aligned} \lambda_{\text{vac.}} - \lambda_{\text{air}} &= n\lambda_{\text{air}} - \lambda_{\text{air}} \\ &= \lambda_{\text{air}}(n - 1). \end{aligned}$$

It follows that the correction to be added to a wave-length in air in order to obtain the value in vacuo is given by the product of the wave-length in air into the refractivity $(n - 1)$ of air for that wave-length. The most accurate measurements for the refractivity of air have been made by Meggers and Peters [1] who express their results at 0°, 15°, and 30° by the following dispersion formulæ—

$$(n - 1)_0 \times 10^7 = 2875{\cdot}66 + \frac{13{\cdot}412}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}3777}{\lambda^4 \times 10^{-16}}$$

$$(n - 1)_{15} \times 10^7 = 2726{\cdot}43 + \frac{12{\cdot}288}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}3555}{\lambda^4 \times 10^{-16}}$$

$$(n - 1)_{30} \times 10^7 = 2589{\cdot}72 + \frac{12{\cdot}259}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}2576}{\lambda^4 \times 10^{-16}},$$

λ being expressed in Ångströms.

Meggers and Peters give a table of corrections which may be used in reducing wave-lengths to vacuum at 15° (see Table, p. 128). In making the correction to vacuum there is one point to be remembered. All measurements of wave-length, except in the case of secondary standards, are made by interpolation methods, when, of course, both standard and

[1] *Astrophys. J.*, 50, 56 (1919); Bureau of Standards, Scientific Papers No. 30, 327 (1918).

unknown wave-lengths are necessarily compared at the same temperature. Since both are equally effected by changes in temperature of the air, any measurements made will be the same as if actually made at the standard temperature of 15°. No necessity arises therefore for temperature correction and whatever may be the actual temperature of the laboratory during the observations, the reduction of the measurements to vacuum must be made with the help of the refractivity of air at 15°.

CHAPTER III.

THE SLIT, PRISMS, AND LENSES.

The Slit.—As generally used at the present time the slit is formed between two metal jaws, one of which is fixed whilst the other is moved by a fine-pitched screw, which enables the width of the opening between the jaws to be accurately adjusted. Each of these jaws is fitted into two parallel grooves cut in a metal frame, this plan being adopted in order to ensure the parallelism of the slit opening. Many designs of mounting the jaws have been produced, but perhaps the best and simplest is that shown in Fig. 16 in front and side elevation.

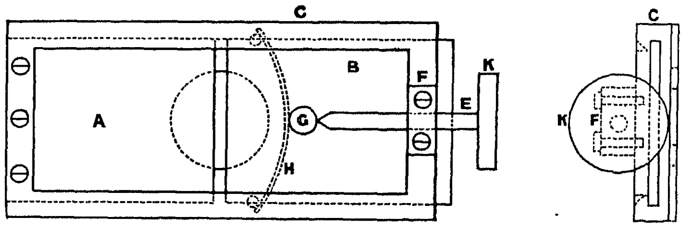


FIG. 16.

The two jaws are shown at A and B, and these are both fitted into two parallel grooves cut along the whole length of the metal frame C. The jaw A is fixed by means of screws into the slit frame, whilst the jaw B is free and is moved by means of the screw E; this screw works in the block F, which is screwed to the slit frame. The pin G, which is fixed into the jaw B, is kept pressed up against the end of the screw E by means of the curved spring H, so that any movement of E forwards or backwards is at once followed by the jaw B. It is of great advantage that the screw E be cut with a definite pitch, either a millimetre or half-millimetre, and that the head of the screw K be graduated, in order that the width of the slit opening may be determined. The spring H should be stiff enough to eliminate all tendency to backlash on the part of the micrometer screw E.

Usually a flat metal plate is screwed to the back of the slit frame, and a central hole is cut in this to admit the passage of the light from the slit; this hole is denoted by the dotted circle in the front elevation diagram in Fig. 16. This design of slit with an oblong frame is adapted for large apertures; very often in smaller apparatus the slit frame is made

circular instead of oblong, but in other respects the design is the same. The round form of frame is convenient for fitting with a cover, which usually consists of a short piece of brass tubing with an end piece containing a glass window. Such a slit cover is useful when working with flame spectra or any source of light which is inclined to bespatter the slit. It must be noted, however, in connection with this round slit frame that much less bearing surface is available for the slit jaws than in the case of the design in Fig. 16.

An improvement on the above form of slit with one jaw fixed is to have both jaws movable and actuated by the same screw. In this design, when any alteration is made in the size of the opening both sides are made to move equally, and thus the centre of the aperture is not displaced. It therefore becomes possible, for example, in comparing the spectra of a bright and a faint source, to use a wider slit in the case of the latter, because the optical centres of the lines are not displaced as they would be in the case of a slit having one jaw fixed.

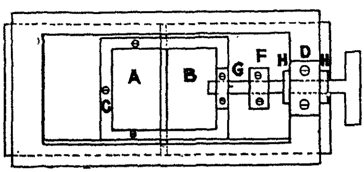


Fig. 17.

Fig. 18.

A diagram of a slit with two movable jaws is given in front elevation in Fig. 17. A and B are the two jaws which are fitted into parallel grooves exactly as in Fig. 16, and the motions of both of them are controlled by a micrometer screw. The parts of this screw which pass through the blocks F and G are screwed with a right- and left-handed thread respectively of equal pitch; the block F is fixed to the jaw B, whilst the block G is fixed to the frame C, which in its turn is screwed to the jaw A. No thread is cut on the screw where it passes through the block D, but a good sliding fit is made and the collars H, H prevent any forward or backward motion. It follows then that when the micrometer screw is turned both jaws are moved at equal rates and in opposite directions.

The frame C is made of the shape shown in order not to obstruct the passage of the light through the slit.

The edges of the jaws of a slit must always be bevelled, as is shown in Fig. 18, with the bevelled edges inside, away from the source of light. The reasons for this are twofold—first, because it is very much easier in this way to obtain edges which are true, and second, because if the edges were not bevelled but cut square a certain quantity of light would be reflected off these edges tending to produce fuzziness in the spectrum lines.

It is essential, of course, for any accurate work that the sides of the slit opening be perfectly true and parallel, as otherwise the diameter of the aperture will vary along its length. In addition to the fact that the edges of the jaws must be cut true and square, it is also necessary that

the jaws move smoothly in their grooves without any trace of side play, and it is for this reason that the long, slit frame shown in Figs. 16 and 17 is to be preferred to any other design; a great length of bearing surface is given to the jaws which minimises the chance of any side play.

A new slit should always be tested for parallelism; this is simply enough carried out by looking through the slit at some source of light, and then slowly closing the aperture by turning the micrometer screw until it just disappears. If properly adjusted the aperture will vanish entirely along its whole length, but if one end closes first, leaving an evidently wedge-shaped opening, the jaws are out of alignment. The readjusting of a bad slit is an extremely delicate and difficult operation, and should only be undertaken by an expert. It must be remembered that the bevelled edges of the jaws are extremely tender and very easily damaged. Great care should be taken never to close a slit tightly, or it may be ruined; then again, in cleaning the edges from dust it is best to use a fine splinter of some dry soft wood such as lancewood, and insert it carefully between the jaws, moving it up and down several times.

As regards the best material for the slit, brass is generally used for the framework and often for the jaws, but in this latter case it is not to be recommended, because it so easily corrodes. The best substance for the jaws is the patent white alloy called platinoid, which is very tough, takes a very high polish, and does not corrode. A very ingenious suggestion came from Crookes in the way of quartz jaws.[1] These jaws are cut in the same way as the metal ones (*vide* Fig. 18), and, therefore, the edges form prisms which refract away all the light which falls on them, so that their transparency or semi-transparency offers no objection. They have the advantage of being able to be worked to a finer edge than the metal jaws, and thus are capable of giving better definition. It is preferable that these jaws should be fitted in grooves outside the jaws of an ordinary slit, as described above, and that they should be so adjusted as to press against the metal jaws; in this way the quartz jaws move with the metal ones simply by friction. The reason for this method of mounting them lies in the fact that the fine edges of quartz are so fragile; there is then little danger of the edges being damaged if by any chance the slit is closed too far.

The dimensions of a slit for any spectroscope are, of course, entirely governed by the size and quality of the lenses and prisms with which it is to be associated; generally speaking the following lengths of aperture may be taken as a basis—with 3-inch lenses a 1 to $1\frac{1}{4}$ inch slit may be used, with 2-inch lenses a $\frac{3}{4}$-inch slit, with $1\frac{1}{2}$-inch lenses $\frac{1}{2}$-inch, and with 1-inch about $\frac{3}{8}$-inch, all being clear aperture; the jaws of a slit are generally made rather wider than the actual aperture is intended to be, and then a diaphragm is placed behind to stop down the aperture to that required. For the dimensions of the whole slit mounting the following may be taken as typical of a slit made for accurate work—

[1] *Chem. News*, 71, 175 (1895).

The slit frame, 95 × 55 mm.
The slit jaws, 48 × 40 mm.
Clear aperture, 30 mm.
Three draw slides (see Fig. 19), each 10 mm. wide.

Micrometer screw for adjusting movable jaw has a pitch of 0·5 mm.

A great convenience may be added to a slit for use with prism apparatus in the shape of draw slides fitted on the front of the slit so as to divide it into sections and obtain several apertures. The great advantage of this arrangement, which is due to Lockyer, in work on the comparison of spectra is obvious. Fig. 19 is a diagram of a slit fitted with three such slides—A, B, and C. These are fitted under a band D, which is screwed to the slit frame; each of the slides can move quite independently of the others, so that as many different spectra can be photographed upon one plate as there are slides.

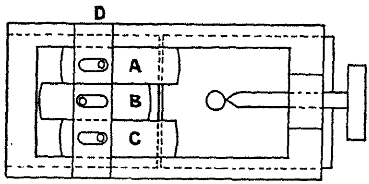


FIG. 19.

In mounting a slit it is best to fit it to a brass tube having a rack-and-pinion arrangement for focusing, as is shown in Fig. 20. A

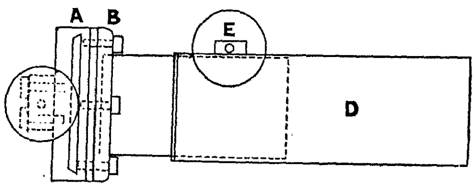


FIG. 20.

is the slit frame with its micrometer screw, and B is a flange which is fitted and screwed to the back of A; into this flange B is screwed a short length of brass tubing which slips into a second piece of tubing D, and is provided with the rack and pinion arrangement E.

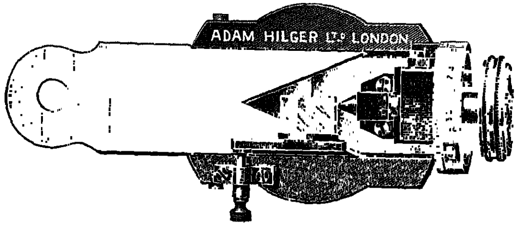


FIG. 21.

One of the most modern forms of slit is shown in Fig. 21, in which the divided drum head and comparison prism can be seen. The instru-

ment is provided with screws whereby any want of parallelism in the slit jaws can be corrected. The length of the slit with full aperture is 18 mm. and this can be reduced by means of the sliding V-shaped diaphragm. A modification of the three draw slides shown in Fig. 19 has now been adopted in the way of three small circular holes cut in a diaphragm which fits in place of the V-shaped diaphragm shown in the figure. These holes are so placed that the three separate spectra obtained by their use are in juxaposition.

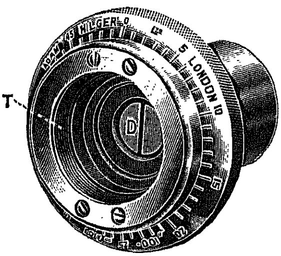


FIG. 22.

A method of obtaining a symmetrically opening slit, different from that shown in Fig. 17, is employed in the slit illustrated in Fig. 22. In this instrument the two jaws are actuated simultaneously in opposite directions by means of the large milled ring. This ring is divided as shown and the width of the slit can be read to 0.001 inch.

The Prism.—The simple theory of the refraction of light by a prism has already been given in the introduction for the case of a single ray; the same relations discussed for that case of course hold good when the prism refracts a beam of light, for the beam may be considered as a bundle of rays, each of which is separately refracted. Evidently therefore the simplest and most satisfactory condition is that the beam consists of a number of parallel rays which are all equally refracted. This condition is generally sought after in prism spectroscopes, and was introduced by Fraunhofer, who was the first to make use of the collimating lens; this lens, as the name suggests, collects the rays coming through the slit and throws them as a parallel beam on to the prism face. If the beam of light passing into the prism is very convergent or divergent, considerable disturbances, arising from aberration, tend to appear which militate against good definition in the spectrum obtained.

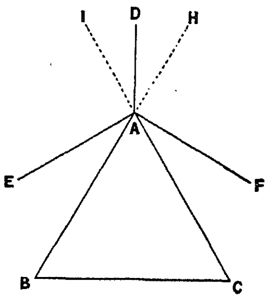


FIG. 23.

The angle contained between the two refracting faces of a prism or the refracting angle, as it is called, which determines to a great extent the amount of deviation produced in the path of a beam of light in its passage through the prism, may be measured as follows. In Fig. 23 ABC represents any prism of which the angle at A is the refracting angle. Let DA mark the direction of a beam of light which falls on the prism; part of this beam will be reflected from the face AB along paths parallel to AE, and part will be reflected from the face AC along paths parallel to AF. Now, if BA and CA be produced to H and I respectively, by the laws of reflection the angles HAD and BAE will be equal

to one another, as also will be the angles IAD and CAF; it follows therefore that the angle IAH is equal to the sum of the angles BAE and CAF. But the angles IAH and BAC are equal to one another, therefore the angle BAC is equal to the sum of the angles BAE and CAF. The whole angle EAF is thus equal to twice the angle BAC.

In order, therefore, to determine the angle BAC it is only necessary to measure the angle between the rays reflected from the two refracting faces of the prism, when a beam of light falls on them as in the diagram, and half the angle found will be the refracting angle BAC. The measurement is carried out quite simply with the help of a spectrometer (*vide* p. 102); the prism is placed on the instrument with the angle which it is required to measure pointing towards the collimator, care being taken that the prism is placed over the centre of the graduated circle. The telescope is then turned until the cross-wires in the eyepiece are exactly adjusted upon the image of the slit as reflected from one face of the prism; the position of the telescope is then read upon the divided circle. The telescope is then turned and adjusted upon the reflected image from the other face of the prism, and if the prism be correctly placed no change of focus of the telescope will be needed. The position is again read, and the difference between the two readings gives the angle through which the telescope has been turned, half of which angle is the angle required.

The method of determining the index of refraction with a prism is due to Fraunhofer, who showed that it can be found for a ray passing through a prism at minimum deviation from the equation—

$$n = \frac{\sin \frac{A + D}{2}}{\sin \frac{A}{2}},$$

where A is the refracting angle of the prism and D the angle of deviation. This equation can be readily proved from the diagram given in Fig. 24.

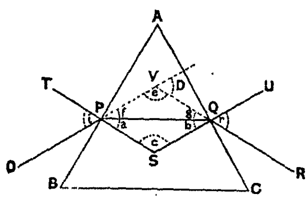


FIG. 24.

Let ABC represent a prism and OPQR the path of a ray at minimum deviation, and which therefore passes symmetrically through the prism. Let TS and US be drawn normal to the refracting faces AB and AC, and let OP and RQ be produced, when D will be the angle of deviation.

It therefore follows that the angles *a* and *b* and the angles *f* and *g* are equal to one another.

In the quadrilateral APSQ the angles APS and AQS are both right angles, and therefore the angles A and *c* are together equal to two right angles.

Again, in the triangle PQS the three angles *a* *b*, and *c* are together equal to two right angles,

therefore $A + c = a + b + c$

and $A = a + b;$

but since $a = b$

therefore $a = b = \frac{A}{2}.$

Now, in the triangle VPQ the three angles e, f, and g are together equal to two right angles, and therefore, since the two angles e and D are together equal to two right angles,

$$e + f + g = e + D$$

and $f + g = D;$

but $f = g$

therefore $f = g = \frac{D}{2}.$

Again, the angle i is equal to the angle VPS, that is, the sum of the angles f and a,

therefore $f = i - a,$

and since $f = \frac{D}{2}$

therefore $i = a + \frac{D}{2} = \frac{A + D}{2}.$

Now, by Snell's law, $n = \frac{\sin i}{\sin a}$, and therefore, by substituting the values found for i and a—

$$n = \frac{\sin \frac{A + D}{2}}{\sin \frac{A}{2}}.$$

This equation is of great value, because the index of refraction can be found from the refracting angle and the minimum angle of deviation, both of which can readily be determined. The method of determining the refracting angle of the prism has been given above, and the angle of deviation is equally easily obtained. The slit of the spectrometer is illuminated with the light the index of refraction for which it is required to determine, and the cross-wires of the eyepiece of the telescope are then adjusted on the image of the slit obtained by direct vision without the intervention of the prism. After the position of the telescope has been read the prism is set in place and the cross-wires of the eyepiece set upon the refracted image; care must, of course, be taken that the prism is set at minimum deviation, this being done by turning the prism round first in one direction and then in the other until the position is found at which the deviation is the least possible. The difference between the two readings is the angle of deviation required.

The above equation, $n = \dfrac{\sin \dfrac{A + D}{2}}{\sin \dfrac{A}{2}}$, will be treated more fully under dispersion and resolving power.

The Total Reflection Prism.—This useful prism is based on the fact, already pointed out (p. 5), that a ray of light cannot pass out from a denser medium into a rarer medium unless the angle of incidence is less than a certain critical angle whose sine is equal to the reciprocal of the relative index of refraction. Such a prism is shown in Fig. 25.

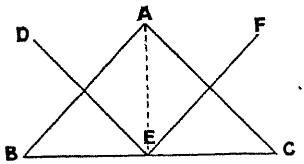


FIG. 25.

ABC is the prism, and DEF the path of a ray of light through it. The angle of incidence of the light on the surface AB is zero, and therefore no refraction takes place; DEA is the angle of incidence on the surface BC, and if this angle be greater than the critical value for the prism substance the whole of the light will be totally reflected and pass out through the face AC, where again there will be no refraction owing to normal incidence. This prism is generally made with the angle BAC a right angle, and the two base angles equal to 45°, since in this way the least amount of light is lost in its passage; when the whole of the face AB is illuminated at normal incidence, it is evident that the whole of the light cannot be totally reflected unless the angle BAC is made equal to a right angle. In this case, therefore, the angle DEA is 45°, and therefore 45° must be greater than the critical angle of the substance employed;

we thus have $$\sin 45° = \frac{1}{n},$$

whence $$n = 1{\cdot}414.$$

It follows from this that a right-angled totally reflecting prism must be made of some substance the index of refraction of which is greater than 1·414. All glasses, however, have indices well above this.

This prism is used in spectroscopy for purposes of the visual comparison of spectra in small instruments; for accurate work, however, recourse should be had to photographic methods, using the draw-slides over the slit shown in Fig. 19, or some similar device. The prism is made to cover one-half of the slit, and by its means light from a side source is reflected in through the slit, whilst the light from another source is directed straight in through the other half of the slit. In this way two spectra may readily be compared.

The total reflection prism is also used in the construction of compound prisms, and trains of prisms as are sometimes made use of in modern spectroscopes. A very ingenious example of the former, which has been introduced by Hilger, is shown in Fig. 26.

This prism consists of two 30° prisms set against the faces of a right-angled totally reflecting prism, and has the property of always giving the same deviation, 90°, when set at minimum, whatever be the index of refraction. The construction of the prism is as follows: ABC is the first prism, of which the angles are: ABC 60°, BAC 30°, and BCA 90°; ACD is an isosceles right-angled prism, so that the angles CDA and CAD are each equal to 45°, whilst the last prism BDE is similar to the first, having the following angles: DBE 30°, BED 60°, and BDE 90°. It thus follows that the two prisms ABC and BDE are each half an ordinary 60° prism.

When a ray of light enters the prism ABC at minimum deviation, making an angle of incidence i at the surface AB, it travels through the prism parallel to the base BC, and enters the prism ACD at normal incidence, and in consequence suffers no refraction. The ray is then totally reflected at the surface AD, and enters the prism BDE at normal incidence, travelling parallel to the base DE, and finally emerges from the face BE, making an angle e with the normal. Since the light traverses both the 30° prisms at minimum deviation, it follows that the angles i and e must be equal to one another, and also, since the two refracting faces AB and BE are at right angles to one another, that the paths of the incident and emergent rays must be at right angles to one another. Thus, whenever in passing through this prism a ray of light is deviated through an angle of 90°, it follows that it travels through at minimum deviation. In practice, therefore, it is simply necessary to fix the collimator and telescope permanently at right angles to one another, when by rotation of the prism round a vertical axis the different portions of the spectrum can be brought into view, that portion seen at any moment having traversed the system at minimum deviation.[1]

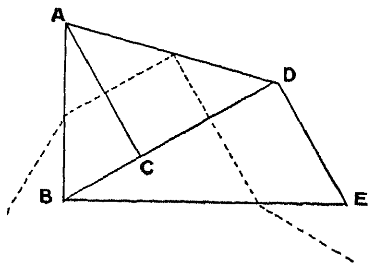


FIG. 26.

There is no need for this prism to be built up actually as described above, and in practice it can be made in one piece in such a way that the four vertical faces enclose four angles equal to 90°, 75°, 135° and 60° respectively.

A spectroscope such as the one just described, in which the collimator and telescope are fixed and the different portions of the spectrum examined by rotation of the prism, is known as a fixed-arm spectroscope. Very many designs of this type of instrument have been made, some of which will be described in the next chapter; some of these are multiple transmission instruments in which the beam of light from the collimator is caused to traverse the same refracting prism a great number of times, finally escaping into the telescope. One of these instruments, designed

[1] See also p. 105.

by Cassie,[1] may be described as a type. It consists of a 30° prism and a right-angled prism cemented together so that the right-angled edge of the latter is perpendicular to the refracting angle of the 30° prism, as is shown in Fig. 27.

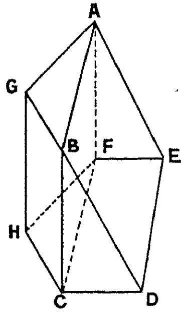


FIG. 27.

ABCDEF is the 30° prism with the right-angled prism AFCBGH cemented against it, though in practice the whole may be cut in one piece. AB is the refracting edge of the 30° prism, and GH is the right-angled edge of the reflecting prism. When the rays pass through this prism at minimum deviation, they fall on the face ABDE, are refracted and travel parallel to the base CD, and on reaching the back are totally reflected and emerge again, parallel to their original path. The prism is used in conjunction with two right-angled prisms, as is shown in elevation and plan in Fig. 28.

The rays from the collimator pass between the two right-angled prisms A and B, as is shown in the elevation, and following the arrows enter the compound prism; they are refracted, and then reflected back and again refracted, as is shown by the arrows in the plan. The rays

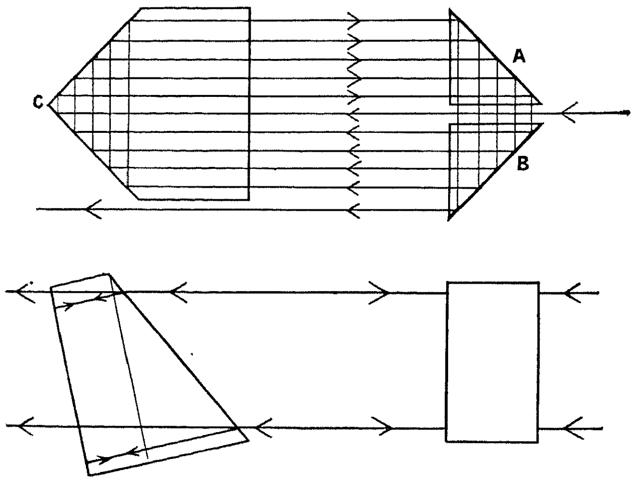


FIG. 28.

travel back along a path parallel to the original path and enter the prism A, and thence by reflection into B, and thence back towards the compound prism C. They thus follow the arrows, going backwards and forwards until finally they pass under the prism C into the telescope. It will be readily seen that this is a fixed-arm spectroscope, with the

[1] Cassie, *Phil. Mag.* (6), 3, 449 (1902). See also p. 107.

collimator at a higher level than the telescope. In order to investigate the various portions of the spectrum it is only necessary to turn the prism C round on a vertical axis, whereby the different regions can be brought into view.

The 30° prism used in the above compound prisms is generally called a half prism, because its shape is that of a 60° prism, cut into two equal portions. This half prism is a very useful instrument, and has been employed for various purposes in different spectroscopes. In certain cases, such as multiple transmission instruments of the fixed-arm type, one face of the half prism is silvered, namely, the face AC in Fig. 29. When a ray of light enters such a prism at minimum deviation, it falls at normal incidence upon the silvered surface, and is therefore reflected back upon its own path. By the use of two such half prisms Cassie has designed a multiple transmission instrument.[1]

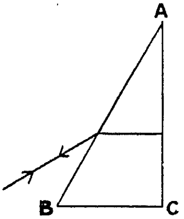


FIG. 29.

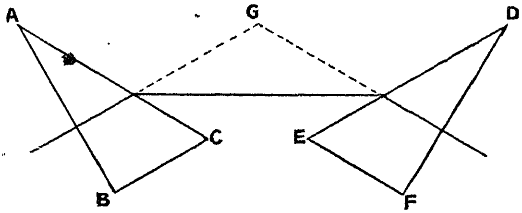


FIG. 30.

The type of half prism made of quartz has been used in the Littrow type of spectrograph for work in the ultra-violet as well as in the visible regions. In such cases, owing to the fact that silver has a very poor reflecting power for ultra-violet light, the surface of the prism is coated with a mercury tin amalgam which is a good reflector throughout the visible and ultra-violet regions.

Thollon[2] made use of a pair of these half prisms in the following way—the two prisms are set with their long faces towards one another, as is shown in Fig. 30, with the path of a ray of light symmetrically through them. One prism, *e.g.* ABC, is fixed so that the face AB is perpendicular to the axis of the collimator, and the other DEF so that the face DF is perpendicular to the axis of the telescope; DEF is fixed to the arm carrying the telescope, so that when the telescope is moved the half prism moves with it. The axis of rotation of the telescope therefore passes through the point G; it can be readily seen from Fig. 30 that as the telescope is moved round the axis G, different parts of the spectrum will come into view, and further, that at all positions of the telescope the ray passing along its axis will have passed through the prisms at minimum deviation. This device was used by Mouton in his work on the indices of refraction of quartz for the infra-red rays.[3]

[1] *Phil. Mag.*, 3, 449 (1902). [2] *Comptes Rendus*, **86**, 595 (1878).
[3] See p. 218.

An important property of the half prism can be seen on reference to Fig. 31, which shows a half prism refracting a beam of light. The diameter of the beam *a* is very much less than the diameter of the beam *b*; the half prism, therefore, can be used in a prism train to diminish or increase the diameter of a beam of light. In this way the full aperture may be employed of prisms which are larger than the aperture of the collimating and telescope lenses; for example, 60° prisms, with an aperture equal to *b* in Fig. 31, can be used with lenses which have only an aperture equal to *a*. Two half prisms are employed, one at each end of the prism train, and in each case the longest faces are turned outwards; in this way, as Rayleigh has shown, greater resolving power can be obtained than would otherwise be possible with a given aperture.[1]

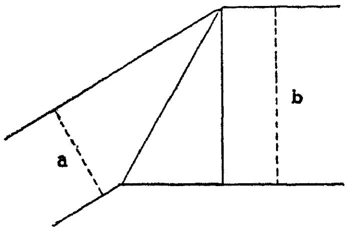


FIG. 31.

Christie has also made use of the half prism in a direct-vision spectroscope.[2]

Dispersion.—If a comparison be made between the values of the indices of refraction for the same rays of light possessed by different substances, it will at once be noticed that the ratios between the indices are by no means the same. For example, in the case of a flint-glass and carbon bisulphide the values for the four rays C, D, F, and H are as follows:—

Line.	Wave-length.	CS_2.	Flint glass.
C	6563	1·618	1·624
D	5893	1·628	1·628
F	4861	1·652	1·641
H	3969	1·689	1·674

Thus the ratio between the indices of carbon bisulphide and the glass is for the D line 1·000, for the F line it is 1·007, and for the H line 1·015. It is evident therefore that, if we had two prisms of exactly the same size, one of carbon bisulphide and the other of flint glass, the deviation suffered by the D line would be the same in each case, but that the F line would be more, and the H line still more deviated by the carbon bisulphide than by the flint-glass prism. We thus see that a change in the wave-length produces a greater change in the deviation in the one case than in the other, or, as it is usually expressed, the value of $\frac{d\theta}{d\lambda}$ is greater for a carbon bisulphide prism than for the glass prism. The

[1] See p. 63.

[2] *Proc. Roy. Soc.*, **26**, 8 (1877).

term $\frac{d\theta}{d\lambda}$, or the ratio of the change in the deviation to the change in the wave-length, is called the dispersion. As a result of the fact that the value of $\frac{d\theta}{d\lambda}$ varies with different substances, it is possible to construct compound prisms for direct vision, and also achromatic lenses. In the first case the prism is so constructed that one ray passes through it undeviated, whilst the others do not, so that a spectrum is still produced; in the second case the converse is true, all the rays are brought to the same focus without destroying the deviation. This second case will be treated under the subject of lenses.

It is quite evident that, if two prisms A and B be taken of the same size and material, and be placed in reversed positions, as in Fig. 32, a ray of light on passing through A will be deviated to a certain extent, and on passing through B will be deviated to exactly the same amount

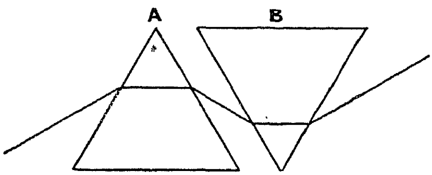


FIG. 32.

in the opposite sense, so that the joint effect of A and B will produce no change in the direction of the ray. If, however, the value of $\frac{d\theta}{d\lambda}$ be different for A and B, then all the rays will not pass through undeviated. For example, let A and B be prisms of carbon bisulphide and flint glass as given above, then clearly a ray of wave-length 5893 will pass through undeviated, but every other ray will be deviated to a small extent; light of wave-length 3969 will be more deviated in the first prism than in the second, and light of wave-length 6563 will be less deviated in A than in B. The result will be that on looking directly through the combination at a source of light a spectrum will be obtained; such a combination is called a direct-vision prism.

In practice it is not convenient to use a carbon bisulphide prism, on account of the difficulty attendant upon the use of hollow prisms filled with liquid, so that two different glasses must be employed, the dispersive powers of which are very different. When, however, this is the case, the indices for one ray are not the same as they are for the D line in the case of carbon bisulphide and glass; this difficulty is readily surmounted by using prisms with different refracting angles. This was first done by Amici in 1860, who used flint and crown-glass, interposing a flint-glass prism between two crown-glass prisms, as is shown in Fig. 33, with the path of the undeviated ray; five prisms, that is, two of flint and three of crown glass, are also often used. Usually the centre

prism (P′ in Fig. 33) of flint glass is now made with a very large refracting angle. This direct-vision combination is especially useful in small pocket spectroscopes; and in these cases a triple combination is usually used, the centre one being made of very dense flint. The prisms are cemented together with Canada balsam; this is both a convenience in construction in order to make them into a single piece of apparatus and also a necessity, as otherwise, in those with wide angles, no light will pass through, owing to the incident angles at the flint prism surfaces being greater than the critical value, so that total reflection would occur. The Canada balsam, as it has a higher refractive index than air, removes this difficulty.

It will be readily understood that the dispersion $\frac{d\theta}{d\lambda}$ is a function of the dispersing apparatus; that is to say, for example, in prismatic spectroscopes it depends both upon the number and the refracting angles of the prisms employed, and also upon the nature of the medium

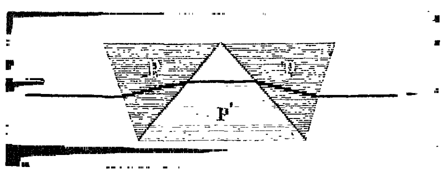


FIG. 33.

out of which the prisms are made. In order, therefore, to calculate the value of $\frac{d\theta}{d\lambda}$ for a prism or prisms, it is necessary to take account of both these factors. In all cases of refraction the deviation produced depends upon and varies with the index of refraction, and, further, the index of refraction varies with the wave-length of the light, so we may therefore put—

$$\frac{d\theta}{d\lambda} = \frac{\delta\theta}{\delta n} \cdot \frac{\delta n}{\delta\lambda} \quad \ldots \ldots \ldots \quad (1)$$

where $\frac{\delta\theta}{\delta n}$ expresses the rate of change in the deviation with change in the index, and $\frac{\delta n}{\delta\lambda}$ expresses the rate of change in the index with change in the wave-length. The factor $\frac{\delta\theta}{\delta n}$ depends, therefore, only upon the angle of incidence and the refracting angle of the prisms, while $\frac{\delta n}{\delta\lambda}$ is solely a function of the medium employed for the prisms. Both these ratios may readily be found.

It has been shown (p. 48) that for a prism at minimum deviation—

$$n = \frac{\sin \frac{A + \theta}{2}}{\sin \frac{A}{2}}$$

where A is the refracting angle of the prism and θ the deviation. Now, by differentiation we find that—

$$\frac{\delta\theta}{\delta n} = \frac{2 \sin \frac{A}{2}}{\cos \frac{A + \theta}{2}}.$$

But, using the same notation as in Fig. 24, p. 48,

$$\frac{A + \theta}{2} = i = \text{angle of incidence},$$

therefore $$\frac{\delta\theta}{\delta n} = \frac{2 \sin \frac{A}{2}}{\cos i}$$

$$= \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \sin^2 i}};$$

but $$\sin i = n \sin a = n \sin \frac{A}{2},$$

therefore $$\frac{\delta\theta}{\delta n} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}}; \quad \cdots\cdots \quad (2)$$

which gives us the value of $\frac{\delta\theta}{\delta n}$ in terms of the prism angle and the index of refraction.

For a 60° prism this is somewhat simplified, as $\sin 30° = \frac{1}{2}$, and therefore in this particular case—

$$\frac{\delta\theta}{\delta n} = \frac{1}{\sqrt{1 - \frac{n^2}{4}}}. \quad \cdots\cdots \quad (3)$$

An example may be given to make this clear.

The value of $\frac{\delta\theta}{\delta n}$ may be calculated for a 60° prism with an index of refraction of 1·5;

we have here, therefore, $\frac{\delta\theta}{\delta n} = \frac{1}{\sqrt{1 - \frac{(1 \cdot 5)^2}{4}}}$

and $$\frac{\delta\theta}{\delta n} = 1 \cdot 512.$$

That is to say, for a very small change in n upon either side of 1·5 the corresponding change in the deviation is 1·512 times as large, provided the prism be set at minimum deviation. For example, let us suppose that n were changed from 1·500 to 1·501, then the value of $\delta\theta$ would be equal to 0·001 × 1·512, which = 0·001512. This, however, is in circular measure, and can be found from tables to be 5′ 15″. In other words, if two rays of light passed through the prism, and if the indices of refraction of the prism material were 1·500 and 1·501 respectively, the difference in deviation suffered by the two rays would be 5′ 15′, that is to say, this would be the angle between the two rays after passing through the prism.

It must be remembered that equations (2) and (3) are only strictly true when the prism is set in the position of minimum deviation, and, therefore, perfectly accurate results can only be obtained when the indices of refraction of the rays in question are very little different from that of the ray at minimum.

In practice, however, the equation can be used over large limits without any great error intervening, and it is then useful in designing a spectrograph for the determination of the angular difference between the extreme rays, and hence the length of the spectrum on a photographic plate. In order to obtain the best approximations over such large limits, it is desirable that the index of the ray at minimum deviation be a mean between the indices of the two rays in question. If the two rays have the indices n_1 and n_2 respectively, then the mean is $\frac{n_1 + n_2}{2}$, which let us call n_3, and we have therefore—

$$\frac{\Delta\theta}{\Delta n} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - n_3^2 \sin^2 \frac{A}{2}}};$$

but Δn now equals $n_1 - n_2$,

therefore $$\Delta\theta = (n_1 - n_2)\left(\frac{2 \sin \frac{A}{2}}{\sqrt{1 - n_3^2 \sin^2 \frac{A}{2}}}\right).$$

This equation is, of course, the more accurate the smaller is $n_1 - n_2$, but the error only amounts to a few minutes when $\Delta\theta$ is as large as 9°.

Thus far the case of one prism only has been considered; it can, however, be proved that $\frac{\delta\theta}{\delta n}$ is simply proportional to the number of prisms, provided they be all of the same size and material. So that if x is the number of prisms we have—

$$\Delta\theta = x(n_1 - n_2)\left(\frac{2 \sin \frac{A}{2}}{\sqrt{1 - n_3^2 \sin^2 \frac{A}{2}}}\right) \quad . \quad . \quad . \quad . \quad (4)$$

and for 60° prisms $= \frac{x(n_1 - n_2)}{\sqrt{1 - \frac{n_3^2}{4}}}$.

For the evaluation of the ratio $\frac{\delta n}{\delta\lambda}$ we can make use of Hartmann's simple interpolation formula.[1] The relation between λ and n can be found from the equations—

$$\left.\begin{aligned} n &= n_0 + \frac{c}{(\lambda - \lambda_0)^a} \\ \text{and} \qquad \lambda &= \lambda_0 + \frac{c}{(n - n_0)^{\frac{1}{a}}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where c, n_0, and λ_0 are constants; a has the value for glass of about 1·2. On putting $a = 1$ we obtain the approximate equations—

$$\left.\begin{aligned} n &= n_0 + \frac{c}{\lambda - \lambda_0} \\ \text{and} \qquad \lambda &= \lambda_0 + \frac{c}{n - n_0} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the latter case we may use the deviation in place of n and write—

$$\lambda = \lambda_0 + \frac{c}{D - D_0}$$

in which case the formula can be used for the interpolation of wave-lengths in a photographed spectrum, if those of certain lines are known. Hartmann tested this formula and found that very good results can be obtained.

By differentiation we obtain the ratio—

$$\frac{\delta n}{\delta\lambda} = -\frac{c}{(\lambda - \lambda_0)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the negative sign simply meaning that a small increase in the value of

[1] *Astrophys. Journal*, **8**, 218 (1898).

λ produces a decrease in the value of n. The equation shows that $\frac{\delta n}{\delta\lambda}$ can at once be found if we know c and λ_0, which are characteristic constants of the dispersing medium. They can be calculated quite easily if the indices of refraction of three rays are known. As an example, we may take a glass (the fluor crown given in the table on p. 77) for which the indices are—

$$n = 1{\cdot}483496 \text{ for } \lambda = 7{\cdot}682 \times 10^{-5} \text{ cm.}$$
$$n = 1{\cdot}490702 \text{ for } \lambda = 5{\cdot}270 \times 10^{-5} \text{ cm.}$$
$$n = 1{\cdot}499605 \text{ for } \lambda = 4{\cdot}046 \times 10^{-5} \text{ cm.}$$

these values give us three equations, from which the following values of the constants are found :—

$$n_0 = 1{\cdot}472247,\ \lambda_0 = 1{\cdot}5070 \times 10^{-5}, \text{ and } c = 6{\cdot}944 \times 10^{-7}.$$

From these constants the values of the indices for the other rays may be calculated and they are given in the following table along with the observed measurements made by Gifford :—

Wave-length in Ånströms.	Indices obs.	Indices calc.
7682	1·483496	(1·483496)
7066	1·484749	1·484738
6708	1·485624	1·485598
6563	1·486012	1·485981
5893	1·488102	1·488079
5607	1·489187	1·489183
5461	1·489823	1·489809
5270	1·490702	(1·490702)
4861	1·492909	1·492951
4678	1·494114	1·494145
4415	1·496091	1·496126
4341	1·496731	1·496749
4046	1·499605	(1·499605)

The maximum error is about 1 in 40,000, which is remarkably good in view of the fact that we have omitted the constant power a from the denominator of the formula. Still better results can be obtained if the three constants, n_0, λ_0, and c, are calculated from three values of the index of refraction for rays which are closer together in the spectrum.

If the constants are known it is possible to calculate the ratio $\frac{\delta n}{\delta\lambda}$ for any substance for light of any wave-length. We have found already that—

$$\frac{\delta n}{\delta\lambda} = -\frac{c}{(\lambda - \lambda_0)^2} \quad \cdots\cdots \quad (8)$$

and as an example let us calculate $\frac{\delta n}{\delta\lambda}$ in the immediate neighbourhood of the F line for the glass dealt with above. We see, therefore, that—

$$\frac{\delta n}{\delta \lambda} = -\frac{6{\cdot}944 \times 10^{-7}}{(4{\cdot}861 \times 10^{-5} - 1{\cdot}507 \times 10^{-5})^2}$$
$$= -617{\cdot}29,$$

which means that, in the neighbourhood of the F line, a small change in λ produces a change in n which is $617{\cdot}29$ times as great.

Similarly $\frac{\delta n}{\delta \lambda}$ may be calculated for any medium with a very close degree of approximation.

We have seen that—

$$\frac{\delta \theta}{\delta n} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}},$$

and as the dispersion $\frac{d\theta}{d\lambda} = \frac{\delta \theta}{\delta n} \times \frac{\delta n}{\delta \lambda}$ we are now in a position to calculate the dispersion for any substance. As an example let us find the angle between the two D lines of sodium after passage through a single $60°$ prism of the glass dealt with above. It is first of all necessary to calculate the value of $\frac{d\theta}{d\lambda}$ in the neighbourhood of the D lines, which for a single $60°$ prism is equal to

$$\frac{1}{\sqrt{1 - \frac{(1{\cdot}488102)^2}{4}}} \times \left[-\frac{6{\cdot}944 \times 10^{-7}}{(5{\cdot}893 \times 10^{-5} - 1{\cdot}507 \times 10^{-5})^2} \right]$$

where $1{\cdot}488102$ is the value of n_D.

We have, therefore, $\frac{d\theta}{d\lambda} = 1{\cdot}4967 \times [-360{\cdot}97]$
$$= -540{\cdot}28.$$

Now, the difference in wave-length ($d\lambda$) between the two D lines, within a sufficient approximation for the present purpose, is 6×10^{-8} cm.; multiplying this by the dispersion we find the angle between the two rays to be—

$0{\cdot}000032417$ radian, or $7''$ very nearly.

In a similar way the dispersion for any substance can be found with a very close degree of approximation. Attention may again be drawn to the fact that, when more than one prism is employed of the same material, the dispersion is simply proportional to the number of the prisms.

The value of $\frac{\delta \theta}{\delta n}$ for a prism train can be expressed in another way, and one that is more convenient for certain purposes.

By differentiation of the formula—

$$n = \frac{\sin \frac{A + \theta}{2}}{\sin \frac{A}{2}},$$

we see that
$$\frac{\delta\theta}{\delta n} = \frac{2 \sin \frac{A}{2}}{\cos \frac{A + \theta}{2}};$$

then, by using the same symbols as upon page 48—

$$\frac{\delta\theta}{\delta n} = \frac{2 \sin a}{\cos i} = \frac{2 \frac{\sin i}{n}}{\cos i},$$

and therefore
$$\frac{\delta\theta}{\delta n} = \frac{2}{n} \tan i;$$

which gives the ratio $\frac{\delta\theta}{\delta n}$ as a function of the angle of incidence on the first prism face.

Another equation which gives n as a function of λ is the well-known one proposed by Cauchy—

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots$$

where A, B, C, etc., are characteristic constants of the medium. This equation is only, however, approximate, yet the simple expression—

$$n = A + \frac{B}{\lambda^2}$$

will give results sufficiently near for many purposes. For example, by differentiation we see that—

$$\frac{\delta n}{\delta\lambda} = -\frac{2B}{\lambda^3},$$

and therefore it can be seen that the ratio $\frac{\delta n}{\delta\lambda}$ is inversely proportional to the cube of the wave-length.

Although the name dispersion has been given to the ratio $\frac{d\theta}{d\lambda}$ in the above, yet the same name is often applied to each of the partial ratios $\frac{\delta\theta}{\delta n}$ and $\frac{\delta n}{\delta\lambda}$.

Resolving Power.—Lord Rayleigh has shown that, in the case of the image of an infinitely narrow slit produced at the focus of a telescope lens, the linear distance ξ of the first diffraction minimum from the principal maximum is defined by the equation—

$$\frac{a\xi}{m\lambda f} = 1$$

where a is the linear aperture of the lens, and f its focal length, and m is a constant varying from 1·0 for rectangular to 1·2 for circular apertures. From this equation we find that—

$$\frac{\xi}{f} = \frac{m\lambda}{a},$$

$\frac{\xi}{f}$ being the angular distance between the principal maximum and the first minimum of the diffraction rings surrounding the main image. Arguing from this, Rayleigh concludes that, in the case of two rays, if we wish to see them separated or "resolved," the least possible angle that can be allowed between them is equal to $\frac{\xi}{f}$. If, therefore, we express the angle between the two rays by $d\theta$, we then see that the minimum condition for resolution is given by—

$$d\theta = \frac{m\lambda}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where λ is considered as the mean wave-length of the pair. We may now investigate how the necessary condition for resolution of two lines can be obtained by means of prisms. As Rayleigh pointed out, the ratio $\frac{\delta\theta}{\delta n}$ for a prism is given by the equation—

$$\frac{\delta\theta}{\delta n} = \frac{s_1 - s_2}{a}$$

where s_1 and s_2 are the thicknesses of the prism material which are traversed by the two extreme rays of the beam. In a properly constructed spectroscope in which the beam of light from the collimator just completely fills the prism, s_2 is zero, and s_1 equals the thickness of the prism base t;

therefore
$$\frac{\delta\theta}{\delta n} = \frac{t}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This may readily be seen to be true from Fig. 34, in which EB $= a$ and BC $= t$.

Now
$$\text{EB} = \text{AB} \cos i = \text{AB}\sqrt{1 - \sin^2 i}$$
$$= \text{AB}\sqrt{1 - n^2 \sin^2 \frac{\text{A}}{2}};$$

again, $$BF = AB \sin \frac{A}{2},$$

and $$t = 2BF = 2AB \sin \frac{A}{2},$$

therefore $$\frac{t}{a} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}};$$

this, however, is the value of $\frac{\delta\theta}{\delta n}$ from Fraunhofer's equation,[1] and thus

$$\frac{\delta\theta}{\delta n} = \frac{t}{a}.$$

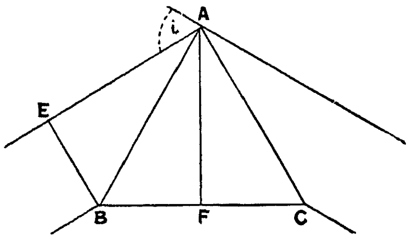


FIG. 34.

Now, by equations (9) and (10) it follows that, for the minimum condition of resolution, omitting the constant m—

$$t = \frac{\lambda}{\delta n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or in other words—in order that two lines may be seen separated in a prism spectroscope, it is necessary that the total thickness of the base of the prism or prisms be equal to the quotient of the wave-length by the difference in the indices of the two lines. As an example of the application of this the necessary value of t for a given resolution may be calculated, and the two D lines of sodium may be chosen; further, the glass dealt with on page 61 may be taken, and the thickness of a prism of this glass calculated which is necessary just to resolve the D lines.

For this glass it was found that $\frac{\delta n}{\delta\lambda} = -360{\cdot}97$,

therefore $$\delta n = 360{\cdot}97 \times 0{\cdot}006 \times 10^{-5},$$

assuming the wave-lengths of the two D lines to be 5896 and 5890 Ångström units respectively;

therefore $$\delta n = 2{\cdot}166 \times 10^{-5}.$$

[1] See equation (2) above.

Then, from equation (11) $t = \dfrac{5\cdot893}{2\cdot166}$ cms.

$$= 2\cdot721 \text{ cms.}$$

In order, therefore, to see the D lines resolved it is necessary, in the case of this glass to use a prism the base of which is at least 2·721 cms. long. Equation (11) shows very clearly that the amount of resolution obtained with a prism depends entirely upon the size of the base; the angle of refraction has no influence, and it follows that all the possible prisms constructed upon the same base as in Fig. 35 give equal resolving power.

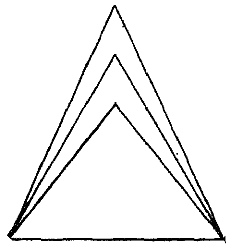


FIG. 35.

When a direct-vision prism system is employed, t in equation (11) must be replaced by $t_1 - t_2$, where t_1 and t_2 are the total thicknesses of the bases of the crown- and flint-glass prisms respectively.

The necessary conditions for resolution may be differently and rather more conveniently expressed; by equations (9) and (10) above, omitting the constant m—

$$d\theta = \frac{t\delta n}{a} = \frac{\lambda}{a},$$

$\dfrac{\lambda}{a}$ being the minimum allowable value of the two first quantities.

Multiplying through by $\dfrac{a}{d\lambda}$ we obtain—

$$a\frac{d\theta}{d\lambda} = t\frac{\delta n}{\delta\lambda} = \frac{\lambda}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where again $\dfrac{\lambda}{d\lambda}$ is the minimum allowable value. Now $\dfrac{\lambda}{d\lambda}$, or the ratio between the mean wave-length of a pair of lines which can just be resolved in a spectroscope, and the difference in wave-length between the two components, is called the *resolving power* of the spectroscope. An instrument which just resolves the D lines is said to have a resolving power of 987. Omitting the constant m, therefore, which is not far from unity, equation (12) shows that the resolving power is equal to the product of the linear (effective) aperture and the dispersion. With a given dispersion, therefore, the resolving power varies directly as the aperture of the apparatus. This is perfectly general, and is true for all dispersing trains, gratings and prisms alike.

The use of the above expression in determining the minimum aperture required for a given resolving power may be illustrated. Let us assume a single 60° prism made of the glass dealt with on page 61 and calculate the minimum aperture necessary just to resolve the D lines. In this case the value of $d\lambda$ is 6×10^{-8} cm. for which the value of $d\theta$ has been found to be $3\cdot2417 \times 10^{-5}$ radian.

We have, therefore,

$$a \times \frac{3\cdot 2417 \times 10^{-5}}{6 \times 10^{-8}} = \frac{5\cdot 893 \times 10^{-5}}{6 \times 10^{-8}}$$

and $a = 1\cdot 818$ cm.

The minimum length of prism base required for résolution of the two D lines in the case of the same glass was shown above to be 2·721 cms. In view of the fact, as will be proved below, that a 60° prism is preferable to any other size it is more convenient to obtain the minimum aperture for resolution rather than the minimum length of prism base.

The resolving power $\frac{\lambda}{d\lambda}$ is usually denoted by the letter r, and, as emphased before, refers to the condition of an infinitely narrow slit and infinitely narrow spectrum lines, that is to say, lines which are perfectly homogeneous; neither of these conditions can be realised in practice, and therefore the practical resolving power differs by a certain amount from the theoretical value obtained from equation (12). The practical resolving power of spectroscopes will be dealt with in Chapter IX.

We have already seen that the ratio $\frac{\delta n}{\delta\lambda}$ varies inversely as λ^3, and therefore it follows that in any prism spectroscope the theoretical resolving power also varies inversely as the cube of the wave-length.

Dimensions of Prisms.—In considering the best dimensions for prisms it is necessary, of course, to take account of the dispersion and the losses of light by reflection and absorption respectively. This has been done by Pickering,[1] who gave tables showing the comparative efficiency of different forms of prisms made from glasses the indices of which are 1·5, 1·6 and 1·7 respectively. The dispersion in these cases may be considered as the ratio $\frac{\delta\theta}{\delta n}$, which has already been shown to be equal to

$$\frac{2 \sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}} \text{ or } \frac{2}{n} \tan i \text{ at the position of minimum deviation.}$$

Loss by Reflection.—It must be remembered that the light refracted by the surface of a medium is partially polarised, and therefore in dealing with the amount which is reflected it is necessary to apply the laws for the reflection of polarised light. Fresnel has shown[2] that in the case of light polarised at right angles to the plane of incidence, if the intensity of the incident ray be put equal to 1, the intensity of the reflected light is equal to $\frac{\sin^2 (i - r)}{\sin^2 (i + r)}$ where i and r are the angles of incidence and refraction; this we may call X. Similarly in the case of light polarised in the plane of incidence the intensity of the reflected light is equal to $\frac{\tan^2 (i - r)}{\tan^2 (i + r)}$, which we may call Y. The amount trans-

[1] *Phil. Mag.* (4), **36**, 39 (1868).

[2] Fresnel, *Œuvres*, tom. 1, pp. 441-479.

mitted, therefore, in each case is equal to $1 - X$ and $1 - Y$. If we regard ordinary light as composed of two beams of equal intensity polarised at right angles to one another, then the amount reflected will be $\frac{X}{2} + \frac{Y}{2}$, and the amount transmitted will be $\frac{1}{2}[(1 - X) + (1 - Y)]$. On meeting a second surface the amount transmitted will be

$$\tfrac{1}{2}[(1 - X)^2 + (1 - Y)^2],$$

and in general for m surfaces $\frac{1}{2}[(1 - X)^m + (1 - Y)^m]$. This formula Pickering applies to a spectroscope in which the prisms are all set at minimum deviation.

These formulæ of Fresnel's, when $i = r = 0°$, that is to say at perpendicular incidence, can both be simplified to the form $\left(\frac{n - 1}{n + 1}\right)^2$, which is of importance in determining the loss by reflection at the surfaces of lenses.

Absorption.—It is well known that when light passes through a medium a certain amount is absorbed; If I_0 denote the intensity of the incident beam and I that of the emergent or transmitted beam, we then will have—

$$\log_e\left(\frac{I_0}{I}\right) = kd$$

where k is a constant depending on the nature of the medium and d is the thickness of the medium. If, then, the intensity of the incident ray be put equal to 1, it follows that the logarithm of the amount absorbed is proportional to the thickness of the medium traversed by the beam.

In the case of prisms d is equal to the average thickness of glass traversed; this is equal to half the base multiplied by the number of prisms which we may put equal to N. Half the base of a prism is, however, equal to $\dfrac{a \sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}}$ where a is equal to the diameter of the aperture at minimum deviation; hence it follows that with an incident beam of intensity $= 1$, the logarithm of the amount absorbed will be proportional to—

$$a \,.\, N \,.\, \frac{\sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}}.$$

But it has already been shown that the dispersion $\frac{\delta n}{\delta \lambda}$ is proportional to $N\dfrac{\sin \frac{A}{2}}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}}$ and therefore the logarithm of the amount of light

absorbed is proportional to the product of the aperture and the dispersion $\frac{\delta n}{\delta \lambda}$. This is an important result, for it means that in spectroscopes of equal dispersion, possessing prisms of the same material, the absorption is the same in all; in other words, it makes no difference to the absorption whether a large number of prisms with small refracting angles or a smaller number with large angles be used, provided both trains have the same $\frac{\delta n}{\delta \lambda}$ and be of the same material. The question of absorption, therefore, does not enter into the question of the best dimensions for prisms.

Pickering has calculated the angles of deviation, the dispersion and the amount of light transmitted by prisms of different angles for the three indices, 1·5, 1·6, and 1·7. His results are given in the following tables. The deviation is, of course, $= 2i - A$.

TABLE I.—45° PRISMS.

	n.	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5	25° 4′	50° 8′	75° 12′	100° 16′	125° 20′	250° 40′
	1·6	30° 30′	61° 0′	91° 30′	122° 0′	152° 30′	305° 0′
	1·7	36° 10′	72° 20′	108° 30′	144° 40′	180° 50′	361° 40′
Dispersion	1·5	0·935	1·870	2·804	3·739	4·674	9·348
	1·6	0·968	1·936	2·904	3·872	4·840	9·680
	1·7	1·008	2·016	3·023	4·031	5·039	10·078
Proportion transmitted	1·5	0·916	0·841	0·774	0·724	0·661	0·461
	1·6	0·892	0·799	0·719	0·651	0·592	0·391
	1·7	0·859	0·745	0·653	0·578	0·516	0·324

TABLE II.—60° PRISMS.

	n.	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5	37° 10′	74° 20′	111° 30′	148° 40′	185° 50′	371° 40′
	1·6	46° 16′	92° 32′	138° 48′	185° 4′	231° 20′	462° 40′
	1·7	56° 26′	112° 52′	169° 24′	225° 44′	282° 10′	564° 20′
Dispersion	1·5	1·512	3·023	4·535	6·046	7·558	15·116
	1·6	1·667	3·334	5·000	6·667	8·334	16·668
	1·7	1·899	3·797	5·696	7·594	9·493	18·986
Proportion transmitted	1·5	0·895	0·811	0·742	0·686	0·641	0·509
	1·6	0·853	0·748	0·672	0·618	0·578	0·491
	1·7	0·801	0·681	0·608	0·565	0·538	0·505

TABLE III.—ANGLES OF PRISMS 67° 22′, 64°, AND 60° 56′.

	n.	Prism angle.	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5 1·6 1·7	67° 22′ 64° 0′ 60° 56′	45° 16′ 52° 0′ 58° 8′	90° 32′ 104° 0′ 116° 16′	135° 48′ 156° 0′ 174° 24′	181° 4′ 208° 0′ 232° 32′	226° 20′ 260° 0′ 290° 40′	452° 40′ 520° 0′ 580° 20′
Dispersion	1·5 1·6 1·7	67° 22′ 64° 0′ 60° 56′	2	4	6	8	10	20
Proportion transmitted	1·5 1·6 1·7	67° 22′ 64° 0′ 60° 56′	0·863 0·818 0·780	0·763 0·702 0·657	0·691 0·629 0·588	0·639 0·582 0·549	0·600 0·552 0·523	0·520 0·505 0·501

By means of these tables the comparative values of the different angles can readily be obtained. For example, three trains of 10 prisms, each with angles of 45°, 60°, and 64°, all being with index 1·6, may be chosen.

	Deviation.	Dispersion.	Light transmitted.
10 prisms of 45°	305° 0′	9·680	0·3911
,, ,, 60°	462° 40	16·668	0·4912
,, ,, 64°	520° 0′	20·000	0·5050

Again comparing trains giving equal deviation—

	Deviation.	Dispersion.	Light transmitted.
12 prisms of 45°	366° 0′	11·616	0·339
8 ,, ,, 60°	370° 8′	13·334	0·532
7 ,, ,, 64°	364° 0′	14·000	0·521

These examples show the superiority of the 60° prism over the 45° prism.

In order to compare the relative values of prisms of different angles, it is preferable to compare together prisms of equal resolving power, as one can then judge more readily their relative merits. If the resolving power be kept constant, but the refracting angle be changed, then the following quantities will vary, the volume of the prism, the length of refracting face, the aperture, the angle of incidence, the loss of light, and the dispersion; the dispersion here being the value of the ratio $\frac{\delta\theta}{\delta n}$.

Wadsworth[1] has calculated these quantities for different refracting angles, the length of base being kept constant, since all prisms of the same glass, with equal bases, have the same resolving power; this has been done for different values of the index of refraction, namely, 1·8, 1·7, 1·6, and 1·5. He first of all gives the values of the volume and of the length of the refracting face of prisms of unit base, which are as follows:—

Refracting angle = A.	Length of refracting face.	Volume of prism.	Refracting angle = A.	Length of refracting face.	Volume of prism.
30°	1·932	0·933	64°	0·943	0·400
35°	1·663	0·793	68°	0·894	0·371
40°	1·462	0·687	72°	0·850	0·344
45°	1·307	0·604	75°	0·822	0·326
50°	1·183	0·536	77·5°	0·799	0·312
55°	1·082	0·480	80°	0·788	0·298
60°	1·000	0·433	82·5°	0·758	0·285

In the four following tables are given the values of the angle of incidence, the aperture, loss of light by reflection, and dispersion $\left(\frac{\delta\theta}{\delta n}\right)$ for prisms of unit base for the indices 1·5, 1·6, 1·7, and 1·8:—

$n = 1·5$.

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	22° 51′	1·780	0·0793	0·5618
35°	26° 49′	1·484	0·0801	0·6738
40°	30° 52′	1·255	0·0815	0·7970
45°	35° 2′	1·070	0·0837	0·9348
50°	39° 20′	0·915	0·0883	1·093
55°	43° 45′	0·782	0·0953	1·278
60°	48° 35′	0·661	0·1047	1·512
64°	52° 39′	0·572	0·1188	1·747
68°	57° 1′	0·487	0·1412	2·054
72°	61° 51′	0·401	0·1795	2·492
75°	65° 57·5′	0·335	0·2280	2·988
77·5°	69° 52′	0·275	0·2938	3·636
80°	74° 37′	0·206	0·4093	4·806
82·5°	81° 30′	0·112	0·6686	8·922

[1] *Astrophys. Journ.*, 2, 264 (1895).

$n = 1·6.$

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	24° 28′	1·758	0·0993	0·569
35°	28° 45·5′	1·458	0·1060	0·686
40°	33° 11′	1·223	0·1083	0·817
45°	37° 45′	1·033	0·1116	0·968
50°	42° 33′	0·873	0·1151	1·145
55°	47° 33′	0·731	0·1274	1·368
60°	53° 8′	0·600	0·1473	1·667
64°	57° 59′	0·500	0·1735	1·999
68°	63° 28′	0·399	0·2213	2·504
72°	70° 12′	0·288	0·3222	3·470
75°	76° 55′	0·186	0·4976	5·378

$n = 1·7.$

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	26° 6′	1·735	0·1214	0·5764
35°	30° 44·5′	1·429	0·1292	0·6998
40°	35° 33′	1·189	0·1358	0·8408
45°	40° 35′	0·992	0·1416	1·008
50°	45° 55·5′	0·760	0·1494	1·315
55°	51° 43′	0·671	0·1665	1·491
60°	58° 13′	0·527	0·1991	1·899
64°	64° 16′	0·410	0·2517	2·441
68°	71° 55′	0·277	0·3731	3·608
72°	88° 28′	0·228	0·9772	4·394

$n = 1·8.$

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	27° 46′	1·709	0·1585	0·5850
35°	32° 46′	1·398	0·1605	0·7152
40°	38° 0′	1·152	0·1643	0·8680
45°	43° 32′	0·900	0·1711	1·111
50°	49° 31·5′	0·768	0·1834	1·302
55°	56° 13′	0·602	0·2100	1·661
60°	64° 10′	0·436	0·2700	2·294
64°	72° 32′	0·283	0·3971	3·532
66°	78° 38′	0·181	0·5675	5·528

Wadsworth has put these values on to curves, and from an inspection of these or the above tables the best value of the refracting angle to be used in any given case can be determined. If the reduction of the angular dispersion be of primary importance, then it is preferable to use

prisms of refracting angles not much exceeding 65° for materials of low refractive index, or 55° for those of high index, since beyond this point any small increase in angle greatly increases the dispersion without decreasing the volume. On the other hand, there is no great gain in reduction of dispersion, and almost none in reduction of loss by reflection, by decreasing the angle below 60°. In the case of a prism for which $n = 1{\cdot}5$, the latter loss is only diminished by about 2·5 per cent. by decreasing the angle from 60° to 30°, while the aperture and dimensions of the spectroscope are increased nearly three times.

If the condition of small dispersion is of less consequence, then it is readily seen that the refracting angle may be increased with decided advantage until it reaches the limit imposed by the diminution of the brightness of the image. When there is plenty of light we may even use angles as large as 80°, in which case the telescopes and other parts of the spectroscope are less than one-third as large as for an angle of 60°, and less than one-eighth those required for a 30° prism. It must, however, be remembered that prisms of wide angles are much more difficult to make than those of small, because of the fact that increased distortion is produced in the spectrum by imperfections in the refracting faces. Very much greater care must be taken in the grinding and polishing of the faces, a fact which increases the cost.

In order that a prism should entirely accept the beam of rays from the collimating lens, it is necessary that the length of the refracting faces should be longer than their height. The height of the prism should be equal to the diameter of the lens; this has been shown on p. 64 to be equal to the length of the face $\times \sqrt{1 - n^2 \sin^2 \frac{A}{2}}$ when in the position of minimum deviation; for 60° prisms the height equals the length of face $\times \sqrt{1 - \frac{n^2}{4}}$.

Thus the length of face $= \dfrac{h}{\sqrt{1 - n^2 \sin^2 \frac{A}{2}}}$ or $\dfrac{h}{\sqrt{1 - \frac{n^2}{4}}}$ for 60° prisms.

We obtain, therefore, the following lengths for prisms of 60°—

$n = 1{\cdot}5$ length = height × 1·51
$n = 1{\cdot}6$ length = height × 1·67
$n = 1{\cdot}7$ length = height × 1·89
$n = 1{\cdot}8$ length = height × 2·29.

The Curvature of Spectrum Lines as produced by Prisms.—It will always be found that the spectrum lines as seen in a prism spectroscope are curved, with the convex sides turned towards the red end of the spectrum. This is due to the fact that only the rays from the centre of the slit pass through a principal plane of the prism; by a

principal plane is meant a plane perpendicular to the plane of the refracting edge of the prism. All cases of refraction through a prism have hitherto been dealt with on the assumption that the rays pass through a principal plane. It can be proved that in order that the deviation be a minimum, it is necessary that two conditions be satisfied, first, that the rays pass through a principal plane, and second, that the angles of incidence and emergence be equal, as has already been stated. The collimator lens is only able to render parallel the rays it receives from the centre of the slit, and therefore these rays only traverse principal planes of the prism; the rays from the other portions of the slit thus do not traverse a principal plane, and therefore suffer a greater amount of deviation, an amount which increases the further from the centre of the slit the rays start. The lines are, therefore, curved when seen with an eyepiece or received on a photographic plate, their ends being bent towards the violet end of the spectrum.

Materials for Prisms.—The media usually employed for prisms are as follows: carbon bisulphide, glass, quartz, Iceland spar or calcite, fluorite, sylvin, and rock-salt. Of these, glass is, of course, the most common, owing to its cheapness and also great variety in its dispersive power. Carbon bisulphide has a very high dispersive power, but is very inconvenient, owing to its being a liquid; quartz, Iceland spar, and fluorite are used on account of their great transparency to the ultra-violet rays, whilst rock-salt and sylvin are useful for their transparency to the infra-red portion of the spectrum.

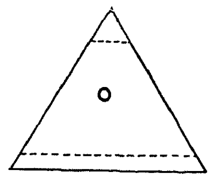


FIG. 36.

Carbon bisulphide, when used, must, of course, be enclosed in a hollow prism, which must be kept well closed on account of the great volatility of the liquid. The hollow prism may be made in various ways; usually a glass prism is moulded, approximately with an angle of 60°, and with a hollow core, as is shown in Fig. 36. The faces are then carefully worked to the 60° angle, and plane-parallel plates of glass are cemented on, best with a mixture of glue and treacle. A hole, of course, must be drilled in the top of the prism for the admission of the liquid; this hole has a stopper accurately ground to fit it, which is cemented in after the prism has been filled. The use of a carbon bisulphide prism is not to be recommended, on account of the disturbances which are inclined to be produced in the spectrum as a result of temperature changes. The index of refraction changes rapidly with temperature; the value of $\frac{dn}{dt}$ lies between 0·00076 for $\lambda = 7600$ and 0·00091 for $\lambda = 4000$, so that very considerable distortions tend to be produced, owing to convection currents in the liquid.

The indices of refraction are given in the following table (Flatow [1]).

[1] *Ann. der Phys.*, **12**, 85 (1903).

λ in A.	− 10°.	0°.	20°.	40°.
6707·87	—	—	1·61678	—
6562·82	—	—	1·61837	—
5892·94	1·65139	1·64362	1·62761	1·61115
5338·3	1·66286	1·65506	1·63877	1·62191
5085·89	1·66974	1·66187	1·64541	1·62842
4861·39	—	—	1·65252	—
4799·91	1·67931	1·67131	1·65466	1·63733
4678·15	1·68420	1·67606	1·65923	1·64181
4415·68	1·69684	1·68850	1·67135	1·65323
4340·37	—	—	1·67515	—
3944·03	1·72888	1·71989	1·70180	1·68278

The dispersive power can be obtained from the differences in the values of the index for the different rays, which are as follows at 20° :—

Complete dispersion.	Partial dispersion.		
6708 to 4340	6708 to 5893	5893 to 4861	4861 to 4340
0·05837	0·01083	0·02491	0·02263

Another liquid which has a great advantage over carbon bisulphide on account of its being much less volatile is monobromonaphthalene. The indices of refraction of this substance are as follows (Bruhl [1]) at 19°.

6707·87	6562·82	5892·94	5350·49	4861·39	4340·37
1·64838	1·64995	1·65876	1·66902	1·68245	1·70433

The dispersion of this liquid is as follows—

Complete dispersion.	Partial dispersion.		
6708 to 4340	6708 to 5893	5893 to 4861	4861 to 4340
0·05595	0·01038	0·02369	0·02188

The dispersion of monobromonaphthalene is, therefore, a little smaller than that of carbon bisulphide, but the change in the index with temperature is much smaller. The value of $\frac{dn}{dt}$ for the former is about 0·00045 throughout the visible spectrum.

Rubens [2] has measured the indices of carbon bisulphide for the infra-red rays, with the following results :—

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·777	1·6104	1·164	1·5960
0·823	1·6077	1·270	1·5940
0·873	1·6049	1·396	1·5923
0·931	1·6025	1·552	1·5905
0·999	1·6000	1·745	1·5888
1·073	1·5978	1·998	1·5872

[1] *Zeitsch. phys. Chem.*, **22**, 373 (1897).

[2] *Ann. der. Phys.*, 45, 238 (1892).

Generally speaking, glass is the best material to use for prisms, unless it be desired to work with the ultra-violet, or extreme infra-red. The advantage of glass lies in its cheapness, and also its toughness; and, further, it is now made in very many varieties, which differ greatly in dispersive power.

In the following tables are given the optical constants for a few of the many glasses made by Messrs Schott and Co. of Jena. In the first table are given the indices of refraction for the following rays:—

A′ $7{\cdot}685 \times 10^{-5}$ cm.	F $4{\cdot}861 \times 10^{-5}$ cm.
C $6{\cdot}563 \times 10^{-5}$ cm.	g $4{\cdot}359 \times 10^{-5}$ cm.
D $5{\cdot}893 \times 10^{-5}$ cm.	h $4{\cdot}047 \times 10^{-5}$ cm.
e $5{\cdot}461 \times 10^{-5}$ cm.	

The second table contains the values of the so-called dispersions of the same glasses, the dispersion being the name used in the glass industry for the difference between the indices of refraction for certain selected rays. The third column of the table contains the values of the medium dispersion, $n_F - n_C$, the brightest rays of the visible spectrum all lying between the two rays C and F. The relative dispersion of a glass is given by $\frac{n_D - 1}{n_F - n_C}$ and the reciprocal of this, commonly designated by ν, is given in the fourth column. The next five columns contain the values of the partial dispersion and in the last column is given the specific gravity; the number under each value of the partial dispersion is the ratio of that partial dispersion to the medium dispersion. These ratios and the values of ν define at once the relative dispersive powers of the various glasses, and they are of great importance in the achromatisation of lenses, as will be more fully explained when we deal with these instruments.

Type.	Description.	A′.	C.	D.	*e*.	F.	*g*.	*h*.
BaLK3	Barium silicate crown	1·51373	1·51573	1·51828	1·52040	1·52432	1·52897	1·53282
K7	Silicate crown . .	1·50561	1·50855	1·51106	1·51314	1·51700	1·52159	1·52540
ZK1	Zincosilicate crown	1·52719	1·53036	1·53307	1·53534	1·53955	1·54457	1·54875
BaK4	Barium silicate crown	1·56228	1·56575	1·56875	1·57125	1·57591	1·58149	1·58614
SK6	Dense crown . .	1·60674	1·61045	1·61366	1·61635	1·62136	1·62734	1·63234
BaLF5	Barium light flint .	1·54086	1·54432	1·54730	1·54983	1·55453	1·56019	1·56494
BaF4	Barium flint . .	1·59702	1·60152	1·60550	1·60889	1·61531	1·62318	1·62991
LF4	Ordinary light flint	1·56981	1·57434	1·57833	1·58173	1·58821	1·59616	1·60299
BaSF1	Barium heavy flint	1·61642	1·62134	1·62591	1·62943	1·63739	1·64662	1·65462
SF2	Dense flint . . .	1·63606	1·64210	1·64752	1·65221	1·66122	1·67249	1·68232
SFS1	Densest flint . .	1·89737	1·91038	1·92250	1·93322	1·95448	1·98223	2·00772
KzF2	Telescope flint . .	1·52281	1·52634	1·52935	1·53187	1·53657	1·54220	1·54693
BK1	Borosilicate crown	1·50477	1·50762	1·51002	1·51201	1·51566	1·51999	1·52356
PK1	Phosphate crown	1·49949	1·50221	1·50447	1·50633	1·50973	1·51373	1·51701
BK5	Borosilicate crown	1·49941	1·50222	1·50456	1·50649	1·51002	1·51417	1·51760
ZK5	Zincosilicate crown	1·52765	1·53083	1·53365	1·53604	1·54046	1·54576	1·55018

Type.	n_D.	Medium dispersion.	ν.	Partial dispersion.					Specific gravity.
				A′ to C.	C to *e*.	*e* to F.	F to *g*.	*g* to H.	
BaLK3	1·51828	0·00859	60·3	0·00300 0·349	0·00467 0·543	0·00392 0·457	0·00465 0·541	0·00385 0·448	2·63
K7	1·51106	0·00845	60·6	0·00294 0·348	0·00459 0·543	0·00386 0·457	0·00459 0·543	0·00381 0·451	2·54
ZK1	1·53307	0·00918	58·0	0·00317 0·345	0·00498 0·452	0·00420 0·458	0·00502 0·546	0·00418 0·455	2·70
BaK4	1·56875	0·01015	56·0	0·00347 0·342	0·00550 0·542	0·00465 0·458	0·00558 0·549	0·00465 0·458	3·11
SK6	1·61366	0·01090	56·3	0·00371 0·340	0·00590 0·541	0·00500 0·459	0·00598 0·548	0·00500 0·458	3·61
BaLF5	1·54730	0·01021	53·6	0·00346 0·338	0·00551 0·539	0·00470 0·461	0·00566 0·555	0·00475 0·466	2·98
BaF4	1·60550	0·01379	43·9	0·00450 0·326	0·00737 0·534	0·00642 0·466	0·00787 0·571	0·00673 0·488	3·52
LF4	1·57833	0·01387	41·7	0·00453 0·327	0·00740 0·533	0·00647 0·467	0·00795 0·574	0·00683 0·492	3·20
BaSF1	1·62591	0·01601	39·1	0·00513 0·320	0·00851 0·532	0·00750 0·468	0·00927 0·579	0·00800 0·500	3·72
SF2	1·64752	0·01912	33·9	0·00604 0·316	0·01011 0·529	0·00901 0·471	0·01127 0·589	0·00983 0·514	3·86
SFS1	1·92250	0·04108	20·9	0·01301 0·295	0·02284 0·518	0·02124 0·482	0·02775 0·630	0·02549 0·578	6·67
KZF2	1·52935	0·01022	51·8	0·00353 0·346	0·00553 0·541	0·00469 0·459	0·00563 0·551	0·00473 0·462	2·56
BK1	1·51002	0·00805	63·4	0·00285 0·354	0·00439 0·545	0·00366 0·455	0·00433 0·538	0·00357 0·445	2·48
PK1	1·50447	0·00752	67·0	0·00272 0·362	0·00412 0·548	0·00340 0·452	0·00400 0·532	0·00328 0·436	2·42
BK5	1·50456	0·00780	64·8	0·00281 0·360	0·00427 0·547	0·00353 0·453	0·00415 0·533	0·00343 0·439	2·40
ZK5	1·53365	0·00964	55·4	0·00328 0·341	0·00521 0·540	0·00443 0·460	0·00530 0·550	0·00442 0·459	2·75

The last three glasses are commonly known under the name of Uviol glasses, because they are far more transparent to ultra-violet light than the ordinary type of glass, and for this reason they are used for many purposes in spectroscopy as will be shown in later chapters. The transparency of these glasses to the ultra-violet rays is shown in the following table, the numbers representing the fraction of the radiation that is transmitted by the different thicknesses given.

Wave-lengths in $\mu\mu$.	Glasses PK1 and BK5.			Glass ZK5.		
	1 mm.	1 cm.	1 dm.	1 mm.	1 cm.	1 dm.
405	1·00	0·99	0·95	1·00	0·98	0·96
366	1·00	0·98	0·89	1·00	0·98	0·82
334	1·00	0·94	0·48	1·00	0·84	0·24
313	1·00	0·70	0·12	0·93	0·48	—
302	0·90	0·38	—	0·82	0·18	—
281	0·56	—	—	0·38	—	—

In the following table are given the optical constants of some glasses selected from the list of those manufactured by Messrs. Chance Brothers. In this table the wave-length of G′ is $4·340 \times 10^{-5}$ cm.

No.	Variety.	n_D.	Medium dispersion.	ν.	C to D.	D to F.	F to G′.	Specific gravity.
7423	Fluor crown .	1·4785	0·00682	70·2	0·00202 0·296	0·00480 0·704	0·00363 0·532	2·47
646	Borosilicate crown .	1·5087	0·00793	64·1	0·00237 0·299	0·00556 0·701	0·00445 0·561	2·46
9322	Hard crown .	1·5186	0·00860	60·3	0·00254 0·295	0·00606 0·705	0·00489 0·569	2·62
4873	Dense barium crown .	1·6118	0·01037	59·0	0·00304 0·293	0·00733 0·707	0·00590 0·569	3·56
1066	Zinc crown .	1·5149	0·00890	57·9	0·00265 0·298	0·00625 0·702	0·00506 0·569	2·62
7863	Extra light flint	1·5290	0·01026	51·6	0·00300 0·292	0·00726 0·708	0·00592 0·577	2·56
8653	Light flint .	1·5632	0·01312	42·9	0·00375 0·286	0·00937 0·714	0·00781 0·595	3·07
360	Dense flint .	1·6225	0·01729	36·0	0·00492 0·285	0·01237 0·715	0·01052 0·608	3·64
7972	Very dense flint	1·7566	0·02754	27·5	0·00774 0·281	0·01980 0·719	0·01736 0·630	4·82
3829	Telescope crown	1·5153	0·00858	60·0	0·00254 0·296	0·00604 0·704	0·00485 0·565	2·50
4277	„ flint .	1·5237	0·01003	52·2	0·00295 0·294	0·00708 0·706	0·00575 0·573	2·67

Lastly, some accurate measurements by Gifford[1] of the refractive indices for six glasses may be quoted.

λ in Å.	Fluor crown S. 5897.	Borosilicate crown S. 6107.	Crown of lowest n_D S. 3113.	Silicate crown S. 7181.	Barium silicate crown S. 7714.	Dense flint S. 5403.
7682	1·483496	1·523556	1·505025	1·521432	1·534892	1·602868
7066	1·484749	1·525075	1·506545	1·522924	1·536492	1·605543
6708	1·485624	1·526076	1·507559	1·523986	1·537580	1·607396
6563	1·486012	1·526533	1·508028	1·524465	1·538061	1·608240
5893	1·488102	1·529077	1·510560	1·527078	1·540736	1·612974
5607	1·489187	1·530406	1·511928	1·528429	1·542186	1·615558
5461	1·489823	1·531182	1·512703	1·529212	1·543001	1·617055
5270	1·490702	1·532271	1·513825	1·530359	1·544154	1·619212
4861	1·492909	1·535050	1·516613	1·533214	1·547146	1·624822
4678	1·494114	1·536570	1·518137	1·534801	1·548749	1·627918
4415	1·496091	1·539041	1·520699	1·537401	1·551389	1·633193
4341	1·496731	1·539820	1·521491	1·538204	1·552261	1·634899
4046	1·499605	1·543462	1·525211	1·541964	1·556187	1·642866
$n_F - n_C$	0·006896	0·008517	0·008586	0·008749	0·009086	0·016582
ν	70·775	62·120	59·467	60·246	59·516	39·966

[1] *Proc. Roy. Soc.*, **91A**, 319 (1915).

Rubens has measured the refractive indices for certain glasses in the infra-red, of which the following may be quoted[1] :—

Glass No. S 163.		Glass No. 0·451.		Glass No. 0·1151.	
λ in 10 - 6 metres.	n.	λ in 10 - 6. metres.	n.	λ in 10 - 6. metres.	n.
0·740	1·8696	0·778	1·5665	0·798	1·5132
0·790	1·8660	0·830	1·5652	0·851	1·5121
0·846	1·8616	0·890	1·5638	0·912	1·5110
0·912	1·8579	0·958	1·5623	0·982	1·5098
0·978	1·8542	1·038	1·5608	1·063	1·5087
1·085	1·8515	1·132	1·5594	1·160	1·5075
1·185	1·8483	1·246	1·5580	1·275	1·5060
1·316	1·8446	1·382	1·5561	1·415	1·5045
1·481	1·8418	1·556	1·5540	1·593	1·5025
1·692	1·8381	1·780	1·5514	1·820	1·4985
1·975	1·8337	2·076	1·5477	2·120	1·4956
2·368	1·8281	2·490	1·5430		

In the following table are given the values of $\frac{dn}{dt}$ for certain glasses measured by Pulfrich,[2] at the various regions specified :—

Number of glass.	Mean temperature.	C.	D.	F.	G′.	Relative change in dispersion. $= \frac{-d\nu}{\nu} \times 100$.
S 57	58·8°	1·204	1·447	2·09	2·810	0·0166
0·544	55·1°	0·244	0·281	0·389	0·503	0·0083
0·527	58·3°	−0·008	+0·014	0·080	0·137	0·0079
0·225	58·1°	−0·202	−0·190	−0·168	−0·142	0·0049

The numbers in the columns headed C, D, F, and G′ represent the changes expressed in units in the fifth place of decimals of the indices for 1° C. at the position of the spectrum lines C, D, F, and G′. In the last column the relative change in dispersion is given, which is equal to $\frac{-d\nu}{\nu} \times 100$, where $\nu = \frac{n_F - n_C}{n_D - 1}$.

Gifford determined the values of $\frac{dn}{dt}$ for the six glasses, of which he measured the refractive indices (see table on p. 77) and the following

[1] *Ann. der. Phys.*, **45**, 238 (1892). [2] *Ibid.*, **45**, 609 (1892).

values show the change in the index caused by a rise in temperature from 15° to 16° :—

S. 8897	S. 6107	S. 3113	S. 7181	S. 7714	S. 5403
−0·0000035	−0·0000016	−0·0000036	−0·0000010	−0·0000049	−0·0000025

Fritsch [1] in a preliminary communication gave the following recipe for making a durable glass, which is transparent to the ultra-violet light as far as $\lambda = 1852$. Six grms. of commercial calcium fluoride are mixed with 14 grms. of boron trioxide, both in a powdered form and melted in a platinum crucible. The resulting fluid is then poured out on an unheated sheet of platinum, too rapid cooling being avoided.

In the following table are given the values of the absorptive powers of certain glasses made by Schott & Co.; [2] the values given are the percentage amounts absorbed by 1 cm. of the glasses at the specified regions of the spectrum.

	Nature of glass.	Wave-length in $\mu\mu$.					
		640.	500.	442.	415.	388.	357.
BK1	Borosilicate crown	0·0	0·7	—	1·2	2·5	4·7
SK1	Densest baryta crown	1·6	2·5	3·4	5·2	9·8	35
BaLF3	Light barium flint	—	1·6	—	2·7	6·0	9
BaF3	,, ,,	0·5	0·9	2·1	2·5	8·6	18
F2	Ordinary silicate flint	0·0	0·0	—	4·1	9·6	28
SF2	Dense silicate flint	0·5	0·9	—	6·9	28	41

It is necessary, when work is to be done upon the ultra-violet end of the spectrum, that the prisms should be made of either quartz, calcite, or fluorite. These three substances offer great transparency towards the rays of short wave-length, a transparency which is most marked in the case of fluorite and least in calcite. Fluorite has been found to transmit all the rays as far as the limit $\lambda = 1200$, whilst quartz is transparent to as far as $\lambda = 1850$, and calcite to $\lambda \doteq 2150$.

The dispersion of fluorite is small, as can be seen from the table given below. It is hardly necessary to mention that the colourless Swiss variety is referred to, the ordinary English fluorspar never being found without considerable colour, and, further, rarely transparent.

Refractive Indices of Fluorite.—The following values have been obtained by Sarasin,[3] Carvallo,[4] and Paschen [5] :—

[1] *Phys. Zeitschr.*, **8**, 518 (1907).
[2] Pfluger, *ibid.*, **4**, 429 (1903).
[3] *Comptes Rendus*, **97**, 850 (1883).
[4] *Ibid.*, **117**, 306 (1893); and **116**, 1189 (1893).
[5] *Ann. der Phys.*, **53**, 812 (1894).

λ in 10^{-6} metres.	n.		λ in 10^{-6} metres.	n.	
0·1856	1·50940	Sarasin	1·444	1·42676	Carvallo
0·19881	1·49629	,,	1·4733	1·42653	Paschen
0·20243	1·49326	,,	1·5715	1·42607	,,
0·20610	1·49041	,,	1·6206	1·42592	,,
0·20988	1·48765	,,	1·7680	1·42517	,,
0·21441	1·48462	,,	1·9153	1·42438	,,
0·21935	1·48150	,,	1·9644	1·42412	,,
0·22645	1·47762	,,	2·0626	1·42363	,,
0·23125	1·47517	,,	2·1608	1·42317	,,
0·25713	1·46476	,,	2·2100	1·42297	,,
0·27467	1·45958	,,	2·3573	1·42208	,,
0·32525	1·44987	,,	2·5537	1·42092	,,
0·34015	1·44775	,,	2·6519	1·42015	,,
0·34655	1·44697	,,	2·7502	1·41969	,,
0·36009	1·44535	,,	2·9466	1·41823	,,
0·39681	1·44214	,,	3·1430	1·41704	,,
0·41012	1·44121	,,	3·2413	1·41608	,,
0·48607	1·43713	Paschen	3·5359	1·41378	,,
0·58930	1·43393	,,	3·8306	1·41121	,,
0·637	1·43292	Carvallo	4·1250	1·40850	,,
0·65618	1·43257	Sarasin	4·4199	1·40559	,,
0·68671	1·43200	,,	4·7147	1·40244	,,
0·700	1·43192	Carvallo	5·0092	1·39902	,,
0·71836	1·43157	Sarasin	5·3039	1·39532	,,
0·76040	1·43114	,,	5·5985	1·39145	,,
0·777	1·43096	Carvallo	5·8932	1·38721	,,
0·878	1·42996	,,	6·4825	1·37837	,,
0·8840	1·42996	Paschen	7·0718	1·36808	,,
1·009	1·42904	Carvallo	7·6612	1·35672	,,
1·1786	1·42799	Paschen	8·2505	1·34444	,,
1·187	1·42804	Carvallo	8·8398	1·33079	,,
1·3751	1·42696	Paschen	9·4291	1·31612 [1]	,,

These values can be expressed extremely well by the formula (Paschen):—

$$n^2 = a^2 + \frac{M_2}{\lambda^2 - \lambda_2^2} - k\lambda^2 - h\lambda^4$$

where $a^2 = 2{\cdot}03888$, $M_2 = 0{\cdot}006166$, $\lambda_2^2 = 0{\cdot}0086959$
$k = 0{\cdot}003200$, $h = 0{\cdot}0000029195$.

Quartz and calcite differ from the other materials detailed below in that they are both doubly refracting substances, and further, in the case of quartz account must be taken of the rotation of the plane of polarisation.

[1] This value is the mean of eight observations, two of which differ somewhat from the rest; the mean of the remaining six is 1·31593.

The following values for fluorite have been obtained by Gifford[1]:—

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·7950	1·430639	0·361066	1·445339
0·768245	1·430949	0·330285	1·449071
0·706559	1·431711	0·303421	1·453382
0·6708	1·432258	0·274868	1·459661
0·656304	1·432523	0·257312	1·464773
0·6438	1·432717	0·244586	1·469650
0·589317	1·433854	0·231295	1·475162
0·56071	1·434565	0·226513	1·477543
0·5461	1·434990	0·21944	1·481453
0·52 011	1·435564	0·214445	1·484569
0·486149	1·437067	0·20988	1·487571
0·4800	1·436910	0·20620	1·490259
0·4359	1·439521	0·20242	1·493182
0·434066	1·439626	0·19881	1·496131
0·4046	1·441530	0·19335	1·501226
0·396168	1·442188	0·18522	1·509889

In general, when a ray of light enters a crystal of calcite or quartz is divided into two portions, one of which is refracted according to nell's law, and in the case of the other the relation between the angles f incidence and refraction depends upon the angle of incidence. This henomenon, known as double refraction, was first discovered by rasmus Bartholinus, in 1669, who noticed that objects viewed through crystal of calcite appeared to be double. It has been since found that ll natural crystals, excepting those which belong to the cubic system, xhibit this interesting phenomenon. The ray which obeys Snell's law called the ordinary ray, and the other the extraordinary ray, and oubly refracting substances can be divided into two classes, namely, ıose in which the index of refraction of the extraordinary ray is greater ıan that of the ordinary ray, and those in which it is less. Crystals elonging to the first class are called positive, and those belonging to ıe second are called negative crystals. The following tables give exmples of both positive and negative crystals[2]:—

POSITIVE CRYSTALS.

	n_0.	n_E.
Quartz	1·544	1·553
Potassium sulphate	1·493	1·502
Dioptase	1·667	1·723
Ice	1·306	1·307
Zircon	1·92-1·96	1·97-2·10

[1] *Proc. Roy. Soc.*, **70**, 329 (1902); and **84**, 193 (1910).
[2] Preston, *Theory of Light*, p. 310.

[NEGATIVE CRSYTALS.

	n_0.	n_E.
Iceland spar	1·658	1·486
Tourmaline	1·637-1·644	1·619-1·622
Beryl	1·584-1·577	1·578-1·572
Apatite	1·646	1·642
Sodium nitrate	1·5854	1·3369

From these tables it will be seen that quartz is positive, whilst, on the other hand, calcite is negative. The theory of double refraction was worked out by Huyghens and Fresnel, and cannot, of course, find a place here; suffice it to say, therefore, that since in the case of glass and isotropic substances the form of the wave of light is a sphere, Huyghens assumed that the sphere was also the form of the wave obeying Snell's law in a doubly refracting crystal, *i.e.* the ordinary ray. The form of the extraordinary wave he imagined to be a spheroid, *i.e.* an ellipsoid of revolution, which is the simplest conception next to that of the sphere.

In all doubly refracting crystals there is one, and sometimes two, directions along which double refraction does not take place. These directions are called the optic axes of the crystal; quartz and calcite are both uniaxial, that is to say, there is one direction through these crystals along which there is no double refraction. When prisms, therefore, are made out of quartz or calcite, it is necessary that they be so cut that the rays inside the prism pass along the optic axis of the crystal, because, if not, the double refraction will cause the spectrum lines to be doubled. It has been pointed out (p. 7) that the path of the rays in a prism set at minimum deviation is parallel to the base, and thus it follows that prisms of quartz or calcite should be so cut that the optic axis lies in a principal plane and parallel to the base, in order that the rays at minimum deviation should not undergo double refraction. It so happens that in the case of calcite this is a very wasteful way of cutting the prism, as can be seen by reference to Fig. 37, which represents a calcite crystal. The crystal is a rhombohedron, bounded by six parallelograms, each of which has two angles of 78° 5′, and two of 101° 55′; it will be seen on reference to the diagram that two of the corners of the crystal, and only two, are formed by the intersection of three wide angles. The optic axis lies along the line joining these two angles, and is shown by the dotted diagonal in the figure. The prism must be so cut that the dotted diagonal lies in a principal plane and parallel to the base; this is a difficult operation, because the prism faces are cut at an angle with the lines of cleavage, and, therefore, the crystal is very readily split. The finished prism must also be carefully handled, as it is very

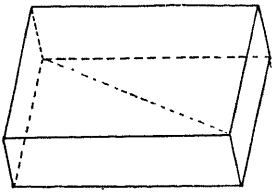


FIG. 37.

easily chipped. In cutting the native crystal it is usual to use a fine copper wire, which has been dipped in a mixture of emery and oil, the wire being drawn backwards and forwards like a saw. Another method of cutting, more applicable for glass, is to use a wheel consisting of a thin disc of copper mounted on a vertical spindle. This disc is rapidly rotated and fine diamond dust or emery, mixed with oil or water, is dropped on to the disc near the spindle. Owing to the rotation the diamond dust or emery is driven to the circumference of the disc, which thus gives a fine cutting edge. The whole is surrounded by a circular screen on to which the excess of the abrasive is thrown and in this way recovered.

Since there is so considerable a difference between the indices of refraction for the ordinary and the extraordinary ray, it follows that double refraction begins to make its appearance when the rays, in passing through a calcite prism, make only a small angle with the optic axis, and, therefore, the spectrum lines will appear sharp only for a very small angular distance on each side of the position of minimum deviation. This entirely militates against the use of prisms of this material for purposes of photographing anything more than very small limits of the spectrum at one time.

The values of the indices of refraction as determined by Gifford are as follows :—

λ in 10^{-6} metres.	n ordinary rays.	n extra-ordinary rays.	λ in 10^{-6} metres.	n ordinary rays.	n extra-ordinary rays.
0·7950	1·648864	1·482165	0·361066	1·693161	1·502235
0·768245	1·649740	1·482552	0·330285	1·705154	1·507458
0·706559	1·652070	1·483532	0·303421	1·719588	1·513646
0·6708	1·653669	1·484271	0·274868	1·741504	1·522662
0·656304	1·654399	1·484569	0·257312	1·760500	1·530121
0·6438	1·655028	1·484680	0·244586	1·779665	1·537310
0·589317	1·658355	1·486392	0·231295	1·802394	1·545500
0·56071	1·660455	1·487345	0·226513	1·813035	1·549144
0·5461	1·661647	1·487890	0·21944	1·830798	1·555122
0·527011	1·663415	1·488706	0·214445	1·845824	1·559923
0·486149	1·667831	1·490741	0·20988	1·860811	
0·4800	1·668613	1·491102			
0·4359	1·675176	1·494104			
0·434066	1·675517	1·494242			
0·4046	1·681343	1·496906			
0·396168	1·683296	1·497774			

In the case of quartz the double refraction is not by any means so pronounced as with calcite; the extraordinary ray is very much weaker than the ordinary ray, and, indeed, is difficult to see. The objection to calcite, therefore, does not apply to quartz, and this substance finds great use in apparatus for photographing the ultra-violet end of the spectrum.

There is, however, a further property appertaining to quartz which must be taken into account, namely, the rotation of the plane of polarisation by a quartz crystal. All doubly refracting substances plane-polarise

the light which they refract, the plane of polarisation of the extraordinary ray being perpendicular to that of the ordinary ray. Quartz, however, in common with certain other substances, has also the power of rotating the plane of polarised light which passes through it, and Biot has shown that the amount of rotation varies directly with the length of path in the crystal.

When light enters a quartz crystal parallel to the optic axis, it is resolved into two rays which are circularly polarised to the right and left respectively. These two rays possess different velocities, and so will be separated and a doubling of the image will ensue. In the case of a 60° prism of quartz cut so that the optic axis lies in a principal plane and parallel to the base the angular distance between the two rays is about 27″ in the neighbourhood of the D lines. Now it has been found that there are two kinds of quartz crystals—right- and left-handed as they are called—in the right-handed variety the dextro-polarised ray, and in the left-handed variety the lævo-polarised ray being less deviated.

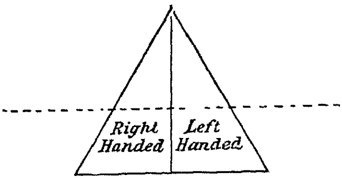


Fig. 38.

It is thus possible, since the two varieties are absolutely similar in their powers, to eliminate entirely the doubling effect by joining together two equal portions of right- and left-handed crystals; the doubling effect produced in the first half is then entirely destroyed in the second. In the case of quartz prisms, therefore, each whole prism is made of two 30° half prisms, one of which is cut from a right-handed and the other from a left-handed crystal, care, of course, being taken that the optic axis is parallel to the base in each half. This method of cutting the prism is due to Cornu, and is shown in plan in Fig. 38.

The indices of refraction of quartz for the ordinary ray were measured by Rubens,[1] who obtained the following values:—

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·19881	1·65070	2·327	1·5156
0·23125	1·61402	2·59	1·5101
0·27467	1·58750	2·84	1·5039
0·31798	1·57290	3·03	1·4987
0·35818	1·56400	3·18	1·4944
0·40458	1·557059	3·40	1·4879
0·43409	1·553869	3·63	1·4799
0·48616	1·549606	3·80	1·4740
0·53496	1·546633	3·96	1·4679
0·58932	1·544147	4·09	1·4620
0·65633	1·541807	4·20	1·4569
0·76824	1·538930	5·0	1·417
1·160	1·5329	5·8	1·368
1·617	1·5272	6·45	1·274
1·969	1·5216	7·0	1·167

[1] *Ann. der Phys.*, **54**, 476 (1895).

These values, excepting the last four, can be expressed by the following equation :—

$$n^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

where $a^2 = 3{\cdot}4629$, $M_1 = 0{\cdot}010654$, $M_2 = 111{\cdot}47$,
$\lambda_1^2 = 0{\cdot}010627$, $\lambda_2^2 = 100{\cdot}77$.

Better results are obtained by the following (Rubens [1]) :—

$$n^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2} - \frac{M_3}{\lambda_3^2 - \lambda^2}$$

where $a^2 = 4{\cdot}57877$, $M_1 = 0{\cdot}010654$, $\lambda_1^2 = 0{\cdot}010627$,
$M_2 = 44{\cdot}224$, $\lambda_2^2 = 78{\cdot}22$, $M_3 = 713{\cdot}55$, $\lambda_3^2 = 430{\cdot}55$.

More recently Gifford [2] obtained the following values for both the ordinary and the extraordinary rays. To these are added the indices for fused silica :—

λ in 10⁻⁶ metres.	*n* ordinary ray.	*n* extraordinary ray.	*n* fused silica.
0·7950	1·538513	1·547421	1·453398
0·768245	1·539060	1·547997	1·453892
0·706559	1·540500	1·549487	1·455180
0·6708	1·541459	1·550472	1·456072
0·656304	1·541931	1·550948	1·456415
0·6438	1·542309	1·551353	1·456771
0·589317	1·544256	1·553366	1·458477
0·56071	1·545475	1·554619	1·459507
0·5461	1·546168	1·555339	1·460155
0·527011	1·547177	1·556388	1·460995
0·480149	1·549700	1·558988	1·463165
0·4800	1·550132	1·559449	1·463571
0·4359	1·553797	1·563227	1·466741
0·434066	1·553976	1·563406	1·466850
0·4046	1·557151	1·566711	1·469675
0·396168	1·558235	1·567836	1·470542
0·361066	1·563473	1·573243	1·475112
0·330285	1·569742	1·579729	1·480610
0·303421	1·576992	1·587231	1·486881
0·274868	1·587529	1·598132	1·496131
0·257312	1·596246	1·607164	1·503707
0·244585	1·604619	1·615860	1·51096
0·231295	1·614034	1·625647	1·519373
0·226513	1·618198	1·629965	1·523053
0·21944	1·624991	1·637022	1·529103
0·214445	1·630466	1·642704	1·533898
0·20988	1·635698	1·648144	1·538547
0·20620	1·640398	1·653037	1·54271
0·20242	1·645584	1·658443	1·54721
0·19881	1·650917	1·663987	1·551990
0·19335	1·660027	1·673488	1·55998
0·18522	1·675895	1·690069	1·5743

[1] *Ann. der Phys.*, **60**, 418 (1897).
[2] *Pro . Roy. Soc.*, **70**, 329 (1902), and **84**, 193 (1910).

Rock-salt and sylvin are used for prisms in cases when the infra-red portion of the spectrum is to be examined. Both these substances being soluble in water are very readily affected by adverse atmospheric conditions, and therefore great care must be taken in their use. The indices of refraction of rock-salt are given in the following table (Rubens [1]):—

ROCK-SALT.

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·434	1·5607	6·78	1·5121
0·485	1·5531	7·22	1·5102
0·589	1·5441	7·59	1·5085
0·656	1·5404	8·04	1·5064
0·840	1·5345	8·67	1·5030
1·281	1·5291	9·95	1·4561
1·761	1·5271	11·88	1·4476
2·35	1·5255	13·96	1·4373
3·34	1·5233	15·89	1·4251
4·01	1·5216	17·87	1·4106
4·65	1·5197	20·57	1·3735
5·22	1·5180	22·3	1·3403
5·79	1·5159		

The following equation expresses these results :—

$$n^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

where $a^2 = 5{\cdot}1790$, $M_1 = 0{\cdot}018496$, $\lambda_1^2 = 0{\cdot}01621$,
$M_2 = 8977{\cdot}0$, $\lambda_2^2 = 3149{\cdot}3$.

Paschen [2] has obtained the following values for the refractive indices of rock-salt :—

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·58932	1·544313	6·4825	1·513628
0·78576	1·536138	7·0718	1·511062
0·88398	1·534011	7·6611	1·508318
0·98220	1·532435	7·9558	1·506804
1·1786	1·530372	8·8398	1·502035
1·7680	1·527440	10·0184	1·494722
2·3573	1·525863	11·7864	1·481816
2·9466	1·524534	12·9650	1·471720
3·5359	1·523173	14·1436	1·460547
4·12524	1·521648	14·7330	1·454404
5·0092	1·518978	15·3223	1·447494
5·8932	1·516014	15·9116	1·441032

[1] *Ann. der Phys.*, **54**, 476 (1895), and **60**, 724 (1897).
[2] *Ibid.*, **26**, 120 (1908).

Rubens[1] found the following values for sylvin :—

SYLVIN.

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·434	1·5048	4·81	1·4705
0·486	1·4981	5·31	1·4695
0·589	1·4900	5·95	1·4882
0·656	1·4868	7·08	1·4653
0·940	1·4805	10·01	1·4561
1·584	1·4761	14·14	1·4362
2·23	1·4745	18·10	1·4162
3·20	1·4727	20·60	1·3882
4·05	1·4716	22·5	1·2692

These values are expressed by the equation—

$$n^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

where $a^2 = 4·5531$, $M_1 = 0·0150$, $\lambda_1^2 = 0·0234$,
$M_2 = 10747$, $\lambda_2^2 = 4517·1$.

Paschen[2] obtained the following values for the refractive indices of sylvin :—

λ in 10^{-6} metres.	n.	λ in 10^{-6} metres.	n.
0·58932	1·490443	5·3039	1·470013
0·78576	1·483282	5·8932	1·468804
0·88398	1·481422	8·2505	1·462726
0·98220	1·480084	8·8398	1·460858
1·1786	1·478311	10·0184	1·45672
1·7680	1·475890	11·786	1·44919
2·3573	1·474751	12·965	1·44346
2·9466	1·473834	14·144	1·43722
3·5359	1·473049	15·912	1·42617
4·7146	1·471122	17·680	1·41403

The values of the temperature coefficient $\left(\frac{dn}{dt}\right)$ of the five last substances are given in the following table (Pulfrich[3]) :—

[1] *Ann. der Phys.*, **54**, 476 (1895) ; **60**, 724 (1897).
[2] *Ibid.*, **26**, 120 (1908). [3] *Ibid.*, **45**, 609 (1892).

Substance.	Mean temperature.	C.	D.	F.	G′.	Relative change in dispersion $= \frac{-dv}{v} \times 100$.
Rock-salt	58·8°	−3·749	−3·739	−3·648	−3·585	0·0148
Sylvin	59·5°	−3·681	−3·641	−3·605	−3·557	0·0143
Quartz ordinary ray	59·6°	−0·649	−0·638	−0·599	−0·577	0·0076
,, extraordinary ray	59·6°	−0·761	−0·754	−0·715	−0·694	0·0071
Fluorspar	60·5°	−1·220	−1·206	−1·170	−1·142	0·0137
Calcite ordinary ray	103°	0·071	0·081	0·091	0·100	0·0137
,, extraordinary ray	103°	1·012	1·020	1·073	1·090	0·0078

In the columns headed C, D, F, and G′ the changes in n for 1° rise in temperature for these rays are given in units in the fifth place of decimals. For example, the value of n for the ordinary ray with quartz is 1·541807 for the C line at a temperature of 15°; at 16° the value of n will be 1·541807 − 0·0000065, or 1·5418005.

Lenses.—In the prism spectroscope two lenses are made use of, one the collimator lens, and the other the telescope lens, the function of the first-named being to collect the rays which come from the slit, and to transmit them as a parallel beam on to the first face of the prism train, whilst the function of the latter is to collect the rays leaving the last prism face, and to bring them to a focus. Then, further, there is the eyepiece, wherewith to examine visually the rays at the focus of the telescope lens. The focal length of a single lens may be found from the well-known equation—

$$\frac{1}{f} = (n - 1)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

where f is the focal length of the lens, n the index of refraction of the given material, and r_1 and r_2 the radii of curvature of the first and second surfaces.

As is evident from this equation, the focal length differs for every ray of different colour, and thus a single lens must give with white light a series of coloured images of different sizes distributed along the axis, or, in other words, a spectrum is produced. The change in the focal length of a lens thus depends upon the dispersion of the material. By differentiation of the above equation we have—

$$d\left(\frac{1}{f}\right) = dn\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

and thus $$d\left(\frac{1}{f}\right) = \frac{dn}{n-1} \cdot \frac{1}{f}$$

$$= \frac{1}{\nu f}$$

if we put $$\nu = \frac{n-1}{dn}.$$

The ratio $\frac{dn}{n-1}$ is known as the relative dispersion of the medium, and may be arrived at in the following way. In the equation for a prism at minimum deviation—

$$n = \frac{\sin\frac{A+\theta}{2}}{\sin\frac{A}{2}}.$$

If the angles A and θ are very small, we may substitute their circular measures for their sines, since the sines of very small angles are proportional to the angles themselves; therefore—

$$n = \frac{A+\theta}{A},$$

whence $$\theta = A(n-1).$$
By differentiation $$d\theta = Adn.$$

Dividing by the previous equation—

$$\frac{d\theta}{\theta} = \frac{dn}{n-1}.$$

By the relative dispersion, therefore, is meant the ratio of the difference in the deviation for two rays in the spectrum to the deviation of one ray taken as standard.

The defect of a single lens, called chromatic aberration, was well known to Newton, who was unable to devise a means of overcoming it in the case of telescopic object glasses, and furthermore said it was impossible to do so; this was because he was ignorant of the difference between the relative dispersions of different materials. For this reason Newton turned his attention to reflecting telescopes.

It is possible, however, to correct the defect by using a double convex lens of crown-glass and a double concave of flint, the two lenses being placed in contact to form the complete lens. By the use in this way of two different kinds of glass, it is possible to bring two different coloured rays to the same focus, but this does not necessarily mean complete achromatism, because the dispersions of the two glasses are not

geometrically similar, and therefore the remaining rays are not absolutely proportional to one another throughout the spectrum; that is to say, the spectra produced by the two glasses are not brought to exactly the same focus as the two chosen rays. There results in this way a small residuary spectrum, which is called the secondary spectrum. Again, by the use of three different kinds of glasses, three chosen rays may be brought to the same focus, leaving a still smaller tertiary spectrum. Usually, however, lenses for spectroscopes are only made of pairs of glasses, because the best firms have succeeded in producing such pairs so perfectly adjusted that their dispersions are almost absolutely proportional; the secondary spectra from lenses of these selected pairs are extremely small, the lenses being perfectly achromatic over a very large portion of the spectrum.

In dealing with the theory of the corrections, it must be noted that there are two errors in an uncorrected lens, which are as follows:—

First, a series of different coloured images is formed along the axis of the lens.

Second, these images are all of different size.

Now, as has already been stated, it is possible, by means of two lenses in contact formed of two glasses with different relative dispersions, to bring two different coloured images to the same focus; therefore, in this case, the second defect will vanish. On the other hand, when the two lenses are not in contact, both the above defects cannot be simultaneously corrected, and it becomes necessary to choose which one shall be corrected.

The condition of achromatism for two lenses in contact, as in the case of the telescopic lens and the collimating lens, may first be considered.

If f_1 and f_2 are the focal lengths of the two lenses respectively, then the relation between the focal length of the pair F is given by the well-known equation.

$$\frac{1}{F} = \frac{1}{f_1} + \frac{1}{f_2}$$

when the rays of light are considered as homogeneous.

In order that the combination be achromatic, it is necessary that the change in the focal length of one lens caused by using light of another wave-length be exactly counteracted by the change in the focal length of the other lens; under these conditions, the focal length of the combination will be the same for the two rays. The necessary condition is evidently given by the equation—

$$d\left(\frac{1}{f_1}\right) + d\left(\frac{1}{f_2}\right) = 0,$$

or

$$\frac{1}{\nu_1 f_1} + \frac{1}{\nu_2 f_2} = 0 \text{ (see p. 89)}$$

when this equation is satisfied, the combination will be achromatic for two rays.

The brightest portion of the spectrum to the eye is included between the C and F rays, and usually, therefore, in apparatus employed for visual work, the lenses are achromatised for these two rays. In the lists of glasses made by the firms of Schott & Co. and Chance Bros., the values of ν for these two rays are given, as may be seen on reference to the tables of selected glasses given on pages 76 and 77. In choosing a pair of glasses for an achromatic lens, it is necessary to select two which differ considerably in values of ν, and then if the above equation of condition be satisfied, a lens can be made which is perfectly achromatic for the two rays of the spectrum known as C and F.

Strictly speaking, such a lens will not be achromatic for the other rays of the spectrum unless the dispersions of the two glasses are geometrically similar throughout the spectrum. In actual fact, however, it has been found possible to make pairs of glasses which, although they differ considerably in their values of ν, still possess very similar partial dispersions. Such a pair of glasses is the following :—

No.	Description.	n_D.	$n_F - n_C$.	ν.	$n_D - n_{A'}$.	$n_F - n_D$.	$n_{G'} - n_F$.
S 30	Dense barium phosphate crown	1·5760	0·00684	65·2	0·00570	0·00622	0·00500
					0·644	0·703	0·565
S 8	Borate flint . . .	1·5736	0·01129	50·8	0·00728	0·00795	0·00644
					0·645	0·704	0·571

These two glasses differ considerably in the values of ν, and their partial dispersions are very similar; for example—

$$\frac{n_D - n_{A'}}{n_F - n_C} = 0{\cdot}644 \text{ and } 0{\cdot}645 \text{ respectively.}$$

$$\frac{n_F - n_D}{n_F - n_C} = 0{\cdot}703 \text{ and } 0{\cdot}704 \quad ,,$$

$$\frac{n_{G'} - n_F}{n_F - n_C} = 0{\cdot}565 \text{ and } 0{\cdot}571 \quad ,,$$

If a compound lens be made of these two glasses, and the equation—

$$\frac{1}{\nu_1 f_1} + \frac{1}{\nu_2 f_2} = 0$$

be satisfied, so that the lens be perfectly achromatic for the C and F rays, then it will also be quite achromatic for the A′ and D rays, and very nearly so for the G′ ray.

A similar pair of glasses, suitable for the object glasses of ordinary

telescopes when achromatism for the three rays C, D, and F is sufficient, is the following:—

		n_D.	Medium Dispersion.	ν.	Partial Dispersion.	
					$n_D - n_C$.	$n_F - n_C$.
K7	Telescope crown	1·5111	0·00845	60·6	0·00251 0·297	0·00594 0·703
KzF2	Telescope flint .	1·5294	0·01022	51·8	0·00301 0·294	0·00721 0·705

As may be readily understood from the above two instances, the achromats produced by the best makers leave very little to be desired. Very often in the case of a telescope lens used for photographing the spectrum, it will be found that the achromatism is perfect from C to F or G, and that for the regions beyond G the lens is a little uncorrected, that is to say, the focal lengths for rays of shorter wave-length than G are rather too small. This may be met in practice by setting the photographic plate at a slight angle, the part intended to receive the blue end of the spectrum being brought a little nearer to the lens. This does not appreciably disturb the focus of the rays at any other part of the spectrum. For example, the telescope lens of one of the spectrographs at the University, Liverpool, has a focal length of 5 feet; the whole spectrum can be photographed in perfectly good focus from C to L by giving a very slight tilt to the plate.

Gifford has found it possible to correct the chromatic aberration of a quartz lens by means of a second lens made of calcite or of fluorite, and exceptionally fine achromatic lenses can be made from these two combinations. These lenses, especially the quartz-fluorite achromat, give an almost perfectly flat field for the whole spectrum to $\lambda = 1850$.

It has also been found possible to produce exceedingly fine achromatic lenses from a combination of quartz and rock-salt. Owing to the danger of atmospheric action on the rock-salt this type of lens is made by enclosing the rock-salt lens between two quartz lenses so that it is entirely protected from the atmosphere. These lenses are now used in some apparatus in place of the quartz-fluorite combination.

The correction for chromatic aberration of a system of lenses separated by an interval cannot be entirely carried out unless each component is separately achromatised. It is only possible, without this, to correct one of the two defects, and it is necessary to choose whether the different coloured images are to be made the same size, or whether they are to be brought to a focus in the same plane. Such a system occurs in eyepieces, and as the eye is a much better judge of size than of distance, the first defect is usually corrected, and the lenses so adjusted that the images are formed all of the same apparent size.

The equation of condition may be found in a similar way to that deduced for two lenses in contact. This equation is as follows [1] :—

$$\frac{x\omega}{f} + \frac{(x+a)\omega}{f^1} = \frac{ax(\omega+\omega^1)}{ff^1}$$

where x is the distance of the object in front of the first lens, a is the distance between the lenses f and f^1 the focal lengths of the two lenses for one ray, and ω and ω^1 the relative dispersions of the two glasses $\left(=\frac{1}{\nu}\right)$.

This equation, however, may be much simplified in the case of an eyepiece, when x is very much larger than a. Hence—

$$\frac{\omega}{f} + \frac{\omega^1}{f^1} = \frac{a(\omega+\omega^1)}{ff^1},$$

and

$$a = \frac{\omega f^1 + \omega^1 f}{\omega + \omega^1}.$$

A great advantage is to be gained by making the two lenses of the same glass, because when corrected for two rays the eyepiece will be perfectly achromatic, therefore we have—

$$\omega = \omega^1,$$

and

$$a = \frac{f^1 + f}{2}.$$

The distance between the lenses must be half the sum of their focal lengths, when the eyepiece, as far as the first defect is concerned, will be perfectly achromatic.

The special form of eyepiece used with a spectroscope is nearly always that known as the Ramsden, which consists of two plano-convex lenses placed with the convex sides towards one another, as is shown in Fig. 39. Both lenses are made of the same focal length, and therefore, in order to secure the best correction for achromatism, the distance between them should be equal to the focal length of either. As in this way the second lens is placed in the focus of the first, the eye sees magnified images of all the defects, such as bubbles in the second lens; the distance between the lenses, therefore, in practice is generally reduced to two-thirds of the focal length, which makes no serious difference to the achromatism, and at the same time throws out of focus to the eye the faults of the second lens.

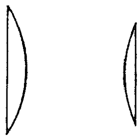


FIG. 39.

The great advantage of the Ramsden form of eyepiece for spectroscopic work lies in the fact that it is used outside the focus of the telescope object glass, so that the eye is enabled to focus a wire or similar object placed in the focal plane of the objective at the same time as the

[1] *Geometrical Optics*, 2nd ed., p. 228. By R. S. Heath. University Press, Cambridge. 1895.

image formed by the objective. The eyepiece fits into an outer tube, which carries a fixed wire or pointer, this pointer being used as an index in measuring the position of a spectral line; in this way the index can be focussed independently of the lines themselves. Usually, two spider webs are used, which are set at an angle to one another, and cross one another in the centre of the field of view; the webs, though excellent

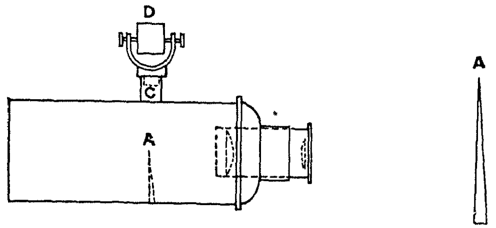


FIG. 40.

when bright lines are being observed, are very difficult to see in the case of faint lines, and it is, therefore, preferable to use a bright pointer. This is best made by grinding the end of a needle flat on one side. The needle is then fixed with the flat side turned towards the eye and a beam of light is thrown on to this pointer from a small mirror, as is shown in Fig. 40.

The pointer is shown at A, and is illuminated by a beam of light directed by the mirror D down the tube C. Care must be taken that the end of the pointer is very fine, and that it can be clearly seen against a black background.

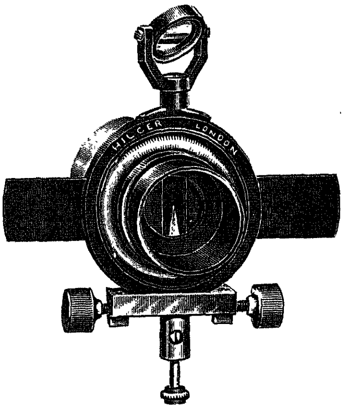


FIG. 41.

In its most complete form the eyepiece is provided with two dark shutters, one on each side, which slide in and out; these are useful to cut off the illumination from any bright lines which may be present on either side of a faint line under observation. The complete eyepiece is illustrated in Fig. 41 and in this instrument the pointer can be moved in either direction across the field of view by means of the two lateral screws shown below the eyepiece.

The micrometer eyepiece is a modified form of the above; in this apparatus the index is made movable, being actuated by a micrometer screw carrying a divided drumhead, by means of which the travel of the index can be measured. These instruments usually have one movable spider web, and also stationary webs fixed across the field parallel to the movable web and distant from one another exactly five or ten threads of

the micrometer screw. They can be used for measuring the distance between the lines in the spectrum visually or on a photographic plate; the readings obtained are, of course, only empirical, and their value must be previously determined, as will be more fully discussed later. The pitch of the micrometer screw is usually 0·5 mm. and one form of this eyepiece is shown in Fig. 42.

For many purposes it is convenient to use lenses which have one face spherically curved and the other face cylindrically curved. Such sphero-cylindrical lenses are very useful as condensing lenses, since the image of a point source is drawn out to a line. Again, such a lens can be employed in the construction of eyepieces, which give great magnification of the spectrum with the loss of as little light as possible. For example, such an eyepiece is made with a magnification of 23 in a horizontal direction and of only 3·85 in a vertical direction. It is obvious that in the ocular examination of the spectra produced by

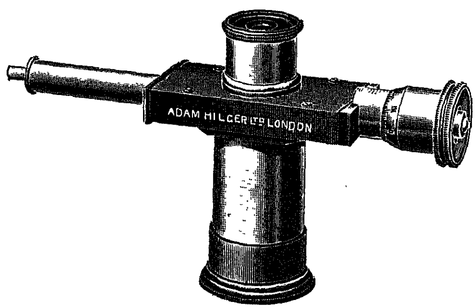


FIG. 42.

spectroscopes of high resolving power, magnification is only required in a direction at right angles to the spectrum lines. Such an eyepiece is admirably adapted for this purpose.

The performance of any spectroscope or spectrograph, as indeed of any piece of optical apparatus, depends naturally upon the accuracy which has been obtained in the manufacture of its optical parts. Thus in any spectroscope or spectrograph it is manifest that the definition and resolving power must depend on the surfaces of the prisms, lenses, and mirrors, which together form the optical system of the instrument. In the description of prisms, for instance, it was tacitly assumed that the refracting faces are perfectly plane; any divergence from this in the way of irregularities of surface must necessarily result in imperfect definition of the spectrum lines obtained.

During recent years the technique of manufacture of optical surfaces, both plane and curved, has improved in a most remarkable way. This very striking advance is in the main due to Michelson and his work on interferometers, since this work may be said to rest on the fundamental basis of truly plane surfaces. The necessity for such surfaces, indeed,

became the mother of invention so that it is now possible to obtain optical surfaces, both plane and curved, with an accuracy of figuring which would never have been obtained but for the pioneer work of Michelson. To a great extent this advance has been due to the English firm of Hilger and indeed Professor Michelson has stated that his measurements would have been impossible had it not been that this firm were able to produce interferometer plates of sufficient accuracy. This work has led to similar improvements in lenses and prism manufacture, and it is obvious that concurrently with such improvements an efficient system of testing the figuring of optical surfaces must be developed. Such a method has been worked out and is in use at the present time. It is not possible here to give a detailed description of the apparatus used, but the principle of the method consists in obtaining interference fringes with an interferometer of the Michelson type (see Vol. II., Chapter I.), one of the light beams passing through the surface under test. The interference bands give a contour map of the surface and from this map the nature of any imperfections can be recognised, that is to say, whether they are in the form of "hills" or "valleys." The treatment of the surface necessary for the removal of these can therefore be determined and a perfect surface obtained. The apparatus and method have been worked out by Twyman.[1]

[1] Interferometers for the experimental study of optical systems from the point of view of the wave theory. *Phil. Mag.*, **35**, 49 (1918); **42**, 777 (1921). *Astrophys. J.*, **48**, 256 (1918). *Trans. Faraday Soc.*, **16**, 208 (1920). *Trans. Opt. Soc.*, **24**, 1 (1922-1923).

CHAPTER IV.

THE COMPLETE PRISM SPECTROSCOPE.

N the last chapter the optical parts of the prism spectroscope—that is, he slit, prism, and lenses—were described in detail; it remains now to reat of their mounting to form the complete instrument. It will be eadily understood that, originating with the simple instrument used by Fraunhofer and modified by Bunsen and Kirchhoff, many methods have been adopted and corresponding designs made depending upon the particular nature of the work to which the instruments were applied. Very ittle use would be served, even if space permitted, by following out the varied forms of spectroscopes that are in use; it is preferable rather to discuss fully the useful types which embody the best notions, and to point out the lines to be recommended to any one who wishes to make or design his own instrument.

The simplest form of spectroscope is the direct-vision instrument, a diagram of which is shown in Fig. 43.

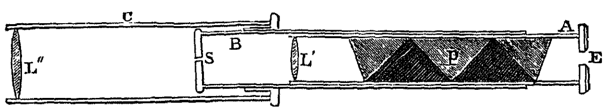


FIG. 43.

This instrument consists of two tubes, A and B, which slide one into the other; the larger of these carries the slit S at one end, and the smaller the prism train P and the lens L′. The slit S in the cheaper instruments is made with fixed jaws, but in those of better quality both jaws are movable, the slit being opened or closed by turning a collar which is fitted round the tube. The lens L′ is an achromat of short focus, and the prism train P in the most recent instruments consists of three prisms, the centre one being of very dense flint-glass. This train is packed into the tube with strips of cork to prevent its slipping. At E a diaphragm is fitted as shown. When in use the instrument is focussed by sliding the smaller tube in or out until the best definition is obtained; in order to prevent the tube carrying the lens and prism train from turning round and getting out of alignment with the slit, a small stud is fixed to the outside of the prism tube A, which works in a slot cut lengthwise in the outer tube B. An accessory is shown in Fig. 43 in the shape of a collimating lens, L″, which is mounted in the tube C. This tube, C,

is made to slide over the tube B in order to allow the rays to be focussed upon the slit.

Sometimes a photographic scale is added to this instrument, the image of which is projected in through a side tube and viewed by reflection from the last prism face. This, however, is only useful for the roughest possible measurements. Such an instrument is shown in Fig. 44.

This instrument is very useful for qualitative examination of spectra, especially in work with vacuum tubes or flames. In the former case, when the vacuum tubes are provided with a capillary portion, as they usually are, there is no need to use a slit, since the narrow column of light can take its place. It is only necessary to look directly at the vacuum tube through the prism train without any lens; this is a very convenient method of working on the spectra of gases, as much greater illumination is obtained.

In spectroscopic work, when it is required to determine the wave-lengths of the lines, recourse must be had to some method of measuring

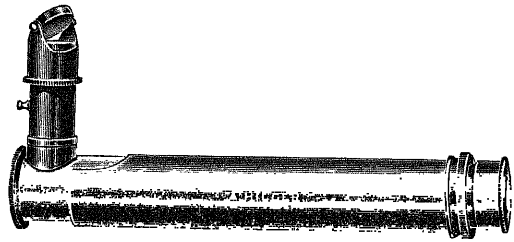


FIG. 44.

their positions in the spectrum. This is always carried out, in the case of prism apparatus and generally with gratings, by measuring the angular deviations of the lines and comparing them with the deviation of lines the wave-lengths of which have already been determined. For very accurate work this is done by means of photography; the two spectra, the standard and unknown, are photographed contiguously one above the other on the same plate, and the wave-lengths of the unknown lines found by measuring their position relatively to the lines in the standard spectrum. This comparison may be made visually, but it is in this case preferable to calibrate the spectroscope beforehand. This latter method is usually adopted for ordinary work, where great accuracy is not required, and where only the visible spectrum is involved. The instrument generally employed is the spectrometer, by means of which the angular deviations of the lines are read directly; it is possible, of course, to use any kind of scale in place of the deviations, because both must be reduced to wave-lengths, but this is not advisable on account of the liability of the arbitrary scale to get out of adjustment.

A diagram of a simple spectrometer is shown in elevation and plan in Fig. 45, but, as will be seen, the stand is omitted; the whole apparatus

in reality firmly screwed to a pillar with a tripod base, each leg of hich has a levelling screw.

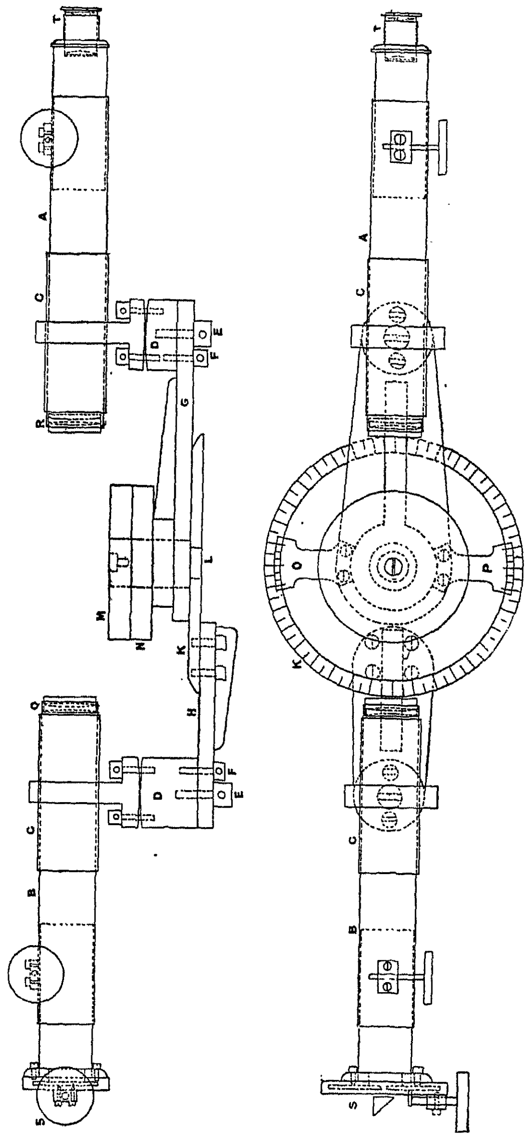


FIG. 45.

In this type of apparatus the telescope is fixed to an arm which is pivoted at the centre of the table of the instrument, and its angular

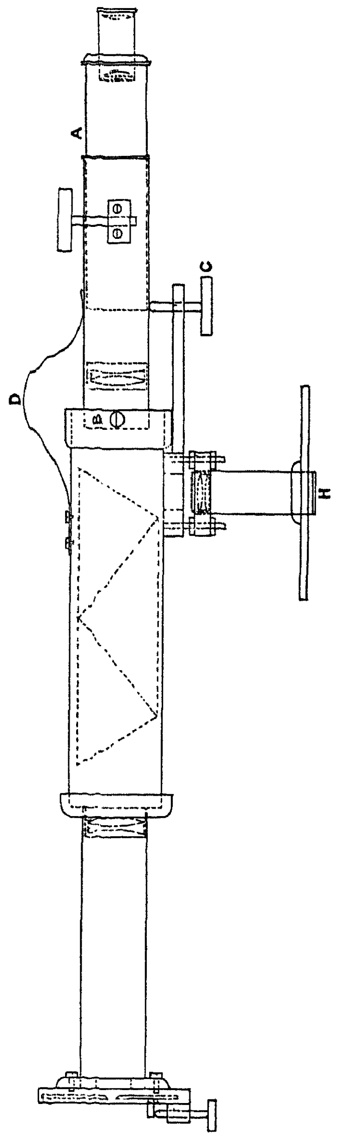


Fig. 46.

movement can be measured on the graduated circle. In the diagram the telescope is shown at A, and the collimator at B, and both fit tightly into the carriers C, C; these carriers are fastened by two screws into the blocks D, D, their bottom surfaces being rounded, as shown, to enable the levels of the collimator and telescope to be adjusted. The blocks D, D are fixed by the screws E, E and F, F to the two arms G and H; the holes cut in these arms, where the screws F, F pass, are elongated to admit of small adjustments to the telescope and collimator in a horizontal plane. Both the arms are strengthened by ribs, as shown, and H, carrying the collimator, is firmly screwed to the central table K, whilst G, carrying the telescope, is accurately fitted to the central steel pin, L, and is free to rotate round it. The prism table M is also made to rotate round the pin L, this motion being useful for bringing the prism into the position of minimum deviation; the lower table N is fixed, and is graduated so that the angular movements of M may be measured if required. The central table K is also divided, and the movements of the telescope are read from the verniers O and P, the accuracy of reading being usually about 30″ of arc. The lenses of the collimator and telescope are shown at Q and R, the slit at S, and the eyepiece at T; both collimator and telescope are provided with rack-and-pinion adjustments for focussing.

A simple measuring instrument has also been made in which a direct-vision prism train is employed, and has been used for ordinary work by Ramsay. A diagram of such an instrument is shown in Fig. 46; the distinguishing feature consists in pivoting the telescope A at the point B so that it is free to move only in a horizontal plane,

which is also a principal plane of the prism system. The motion of the telescope is controlled by the micrometer screw C, a spring D being fixed to keep the telescope pressed up against the end of C. Readings of the positions of the spectrum lines may be read in two ways, either by the graduations on the drumhead of the micrometer screw, using

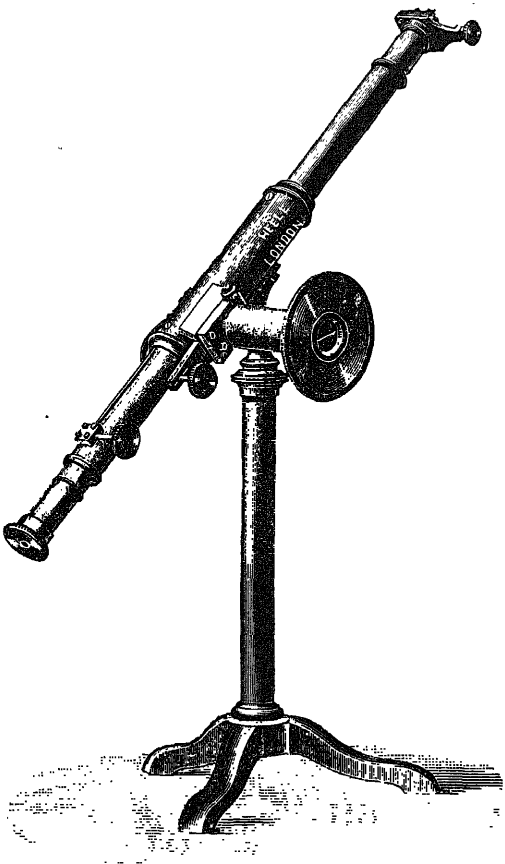


FIG. 47.

some form of index or pointer in the eyepiece, or their positions may be read upon a photographed scale H, seen by reflection from the last prism face.

The complete instrument is shown in Fig. 47.

In the spectrometer shown in Fig. 45 certain faults of construction are evident, and these must be eliminated if an accurate instrument is required. The chief of these is the want of rigidity. For example, the

arms G and H are too slender, as also are the two carriers C and C; a slight pressure of the hand upon the telescope eyepiece during a reading causes a shifting of the spectrum lines, which naturally prevents any accuracy of reading. Though perhaps this instrument is sufficiently rigid for ordinary work, some such design as shown in Figs. 48 and 49 must be employed if any good work is to be done in which the direct measurement of angular deviation is involved.

In the instrument shown in Fig. 48 it will be seen that the telescope is rigidly fastened to the heavy arm A, which is accurately ground on to the central vertical axis, and carries a counterpoise B. The divided circle is 12 inches in diameter, and is read by means of two travelling wire micrometer eyepieces C and D, by means of which the circle divisions can be subdivided to 1″ of arc. Two tangent screw motions

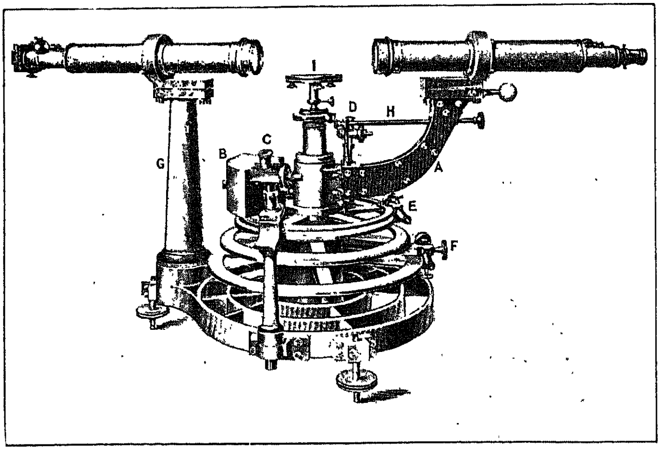


FIG. 48.

E and F are fitted, one for slow adjustment of the arm carrying the telescope and the other for moving the graduated circle round the axis in order to enable readings to be made upon different portions of the graduations; this latter adjustment is used to eliminate any errors of graduation. The collimator is carried by a separate standard G, which forms part of the tripod stand of the instrument. The prism table I can be rotated upon its vertical axis by the rod H, the two being connected by bevel gearing.

Another well-designed spectrometer is shown in Fig. 49. In this instrument the divided circle is 10 inches in diameter and can be rotated so as to eliminate any errors in the graduation. This circle has two sets of graduations on platinoid, one on the top, on which the prism table reads by a vernier to 30″, and one on the edge on which the telescope reads by two microscopes, each with a micrometer eyepiece, to 1″.

Fig. 50 shows a spectrometer made by Hilger for Lieut.-Colonel J. W. Gifford, who has very kindly allowed me to reproduce it. The main features of this instrument are clearly enough shown in the illustration; there are, however, certain details to which it is necessary to draw

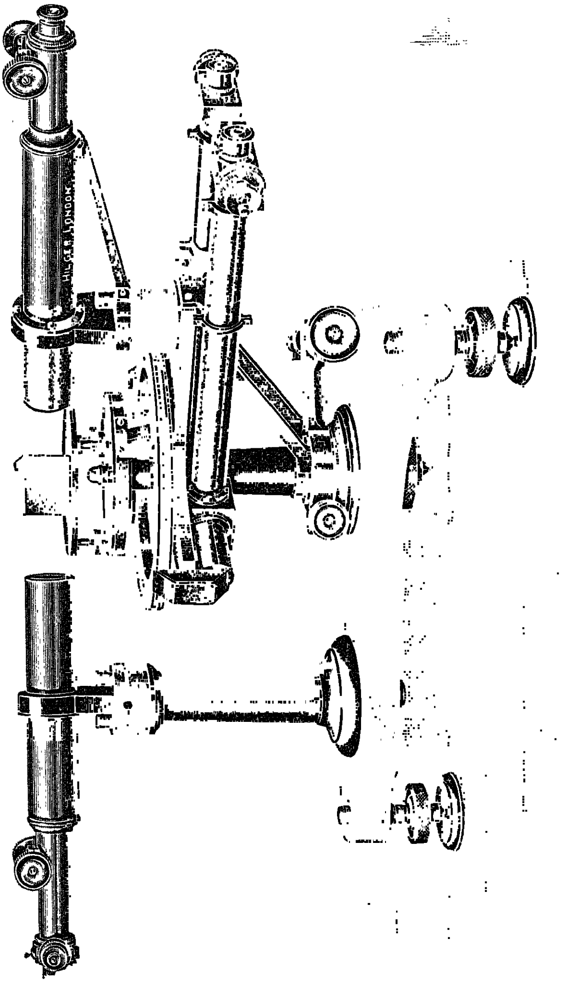


FIG. 49.

special attention. It will be at once noticed that the brass tubes as usually used for the telescope and collimator have been replaced by leather bellows; this is owing to the fact that there is always a slight amount of side-play in the focussing arrangements when brass tubes sliding into one another are used. The adjustments for focussing in this

instrument can be seen underneath the leather bellows, and consist of tongued and grooved metal slides, as long as possible, so as to give plenty of bearing surface. At the eyepiece end of the telescope there is a photographic attachment, as shown in the illustration, and the eyepiece is visible outside the camera box; when used for visual work the dark slide is removed. The main graduated circle of the instrument is 18 inches in diameter, and can be read by means of micrometer eyepieces to within 1″ of arc. The prism table is also graduated, and can be read by means of a short telescope. Both the prism table and the fine adjustment of the telescope can be manipulated from the eyepiece end of the instrument, the former by the handle to be seen just under the telescope bellows, and the latter by the handle under the telescope arm. The key shown at the lower end of the telescope

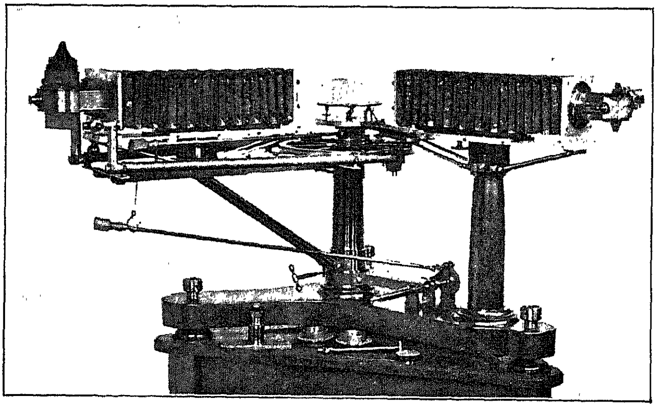


FIG. 50.

bearing, just above the tripod stand, is for the purpose of throwing the fine adjustment in or out of gear.

There is also another type of instrument which may be described here, namely, the fixed-arm spectroscope, although perhaps some of these instruments are not adapted for quantitative work. By a fixed-arm spectroscope is meant an instrument in which the telescope and collimator are immovable, and the spectrum is made to pass along in front of the observer by rotating the prism train. In this type may be included the Littrow instrument, in which the principle of auto-collimation is adopted, that is to say, the same tube serves for both collimator and telescope. The simplest form of fixed-arm spectroscope is one in which the constant deviation prism shown on p. 51 is employed; in this instrument the telescope and collimator are fixed in the same horizontal plane, and at right angles to one another. The constant deviation prism is mounted upon a table which can be rotated by a tangent screw and in this way, as follows from the construction of the

prism, the rays seen through the telescope are always those which traverse the prism at minimum deviation.

Recently this instrument has been improved by Hilger, who has converted it into a direct reading wave-length spectrometer. The prism

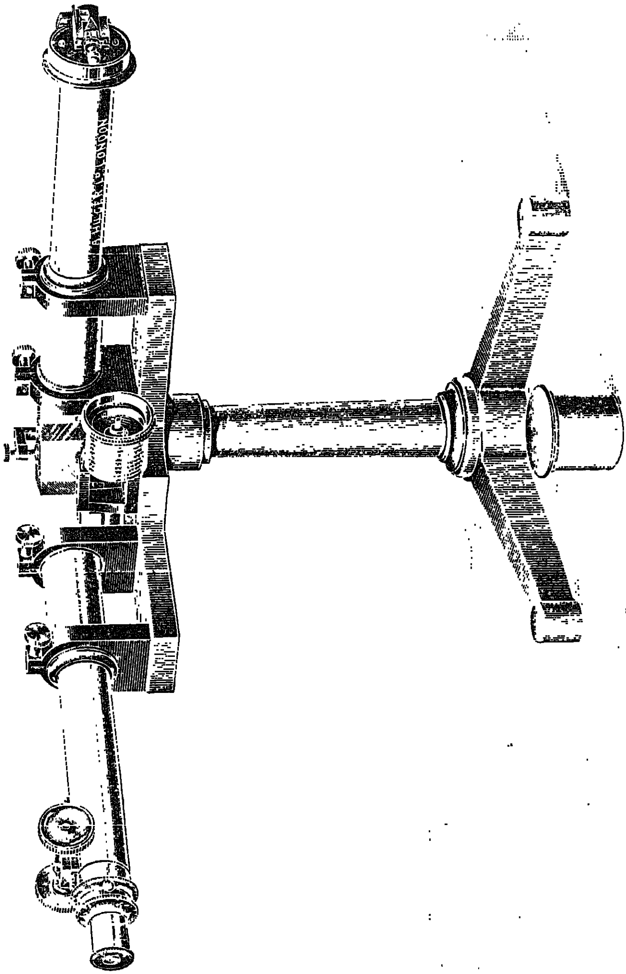


Fig. 51.

table is rotated by means of a tangent screw carrying a drum-head, upon which is a scroll graduated in wave-lengths. The eyepiece carries a spider web, which is adjusted on the spectrum line, and then the wave-length can be read directly off on the drum-head. The spider web itself may be moved a little to either side by means of a small screw projecting

from the eyepiece, so that if at any time the instrument requires adjustment this may readily be carried out. This instrument, although the accuracy is not very great (about two Ångströms), proves exceedingly useful in ordinary spectroscopic work. The instrument is shown in Fig. 51 and as can be seen the telescope is provided with rack and pinion adjustment for purposes of focussing. A more modern adjustment used in this and other apparatus consists of a helical mechanism operated by a milled ring on the body of the telescope. This mechanism moves the telescope lens, the eyepiece remaining fixed, and has considerable advantage since the one-sided thrust given by the rack and pinion is absent.

Another instrument of this type is the one in which the multiple transmission prism system devised by Cassie is used. This prism system was shown on page 52 and, it will be seen, requires the telescope and collimator to be fixed with their axis parallel to one another, but not coincident; the latter must be a little higher than and a little to one side

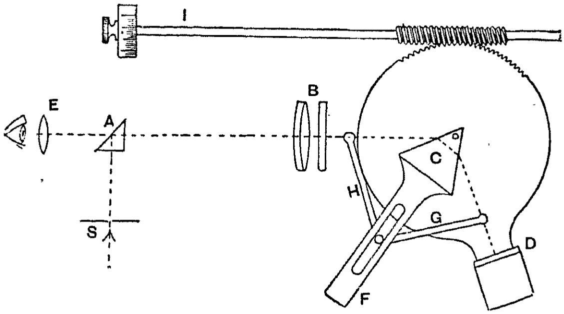


FIG. 52.

of the former, the amount of displacement being determined by the size of the prisms. The spectrum is made to traverse the field of view in the telescope by rotating the prism C (Fig. 28) round a vertical axis. Several other instruments of this type have been devised.

A diagrammatic plan of a Littrow type of spectroscope is shown in Fig. 52. The light enters the slit S, and then is totally reflected by the prism A; the lens B directs it as a parallel beam upon the prism C. This transmits the rays at minimum deviation, and they then fall normally upon the plane mirror D which reflects them back through the prism to the lens B, whence they pass to the eyepiece E. The instrument is so adjusted that the rays on the return journey pass above or below the right angle prism A. At F is shown an arrangement for automatically keeping the prism in the position of minimum deviation; the tie G is pivoted upon the arm carrying the mirror D, which is free to rotate round a vertical axis directly under the centre of the prism C. The tie H is pivoted upon the stand of the apparatus; both the ties G and H are pivoted together to a pin working in the slot in the arm F, which

carries the prism C. In order to cause the spectrum to move across the field of view it is only necessary to rotate the arm carrying the mirror D through a certain angle; it is clear that the prism C will move through half that angle, and therefore will be automatically kept in the position of minimum deviation.

A similar instrument, in which a concave mirror is used in place of the lens B in the last case, has been devised by Wadsworth,[1] and is shown in Fig. 53.

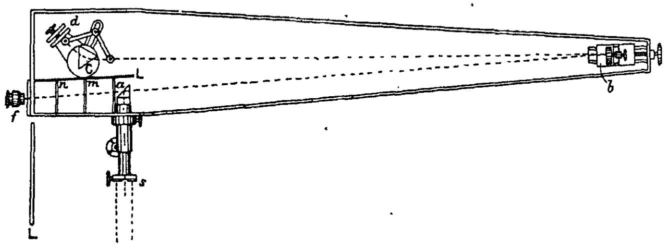


FIG. 53.

In this instrument the light enters the slit at *s*, and is then directed by the right-angle prism *a* on to the concave mirror at *b*; from here the light passes through the prism *c* to the plain mirror *d*. By this mirror it is reflected back along its path, and passing under the prism at *a* it reaches the eyepiece at *f*. As will be seen, the prism at *c* is provided with the same arrangement as in the last apparatus for automatic adjustment in the position of minimum deviation.

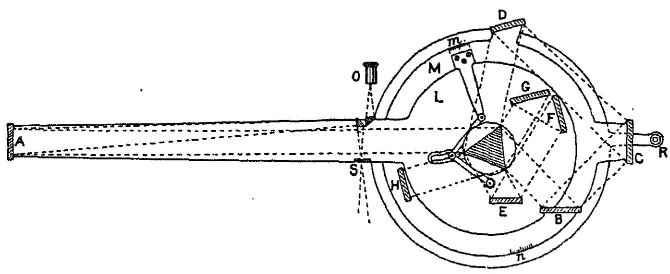


FIG. 54.

Wadsworth[2] has also designed a multiple transmission spectroscope, which partakes of the Littrow type. A diagram is shown in Fig. 54; the light coming through the slit at S is totally reflected by the right-angle prism on to the concave mirror A, by which it is directed as a parallel beam on to the refracting prism. The rays traverse the prism at minimum deviation, and are reflected by the plane mirrors B, C, and D,

[1] *Phil. Mag.*, 38, 137 (1894). [2] *Astrophys. Journ.*, 2, 264 (1895).

and then again enter the prism. On emerging they are again reflected by the plane mirrors E, F, and G, and enter the prism a third time. They then fall upon the plane mirror H, which is placed perpendicularly to their path; they are thus reflected back along their path till they reach the concave mirror A, by which they are focussed through the reflecting prism into the eyepiece at O. The light thus traverses the prism six times, each time at minimum deviation. The method of adjusting the mirrors and refracting prism is automatic, and is obtained as follows. The first set of reflectors, B, C, D, and the final reflector H,

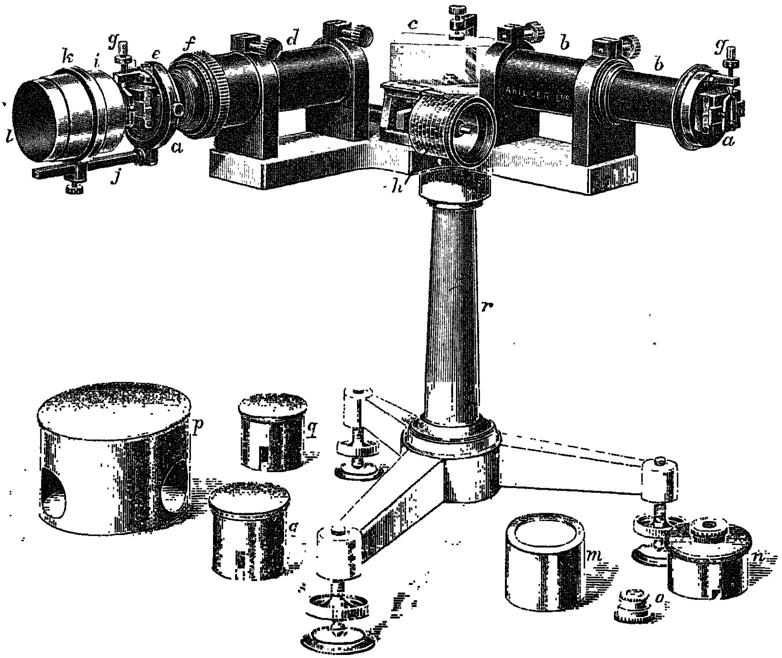


Fig. 55.

are all fixed on the vernier circle M of the spectroscope, and rotate together with it; and the second set of reflectors, E, F, and G, are mounted together on an inner table, fixed to the arm which carries the concave mirror A, slit S, and observing eyepiece or plate-holder O. The prism itself is mounted on a third table, connected with the outer movable table M by means of the usual minimum deviation attachment. The outer divided circle *n* also rotates, and has attached to it an arm R for a small observing telescope, which is used only in the preliminary adjustment.

On account of the great number of reflections that the light has to undergo, this instrument is only suitable where very bright sources can

be employed. At the same time it has the advantage of giving very high resolving power with only one prism, a consideration of some importance if a costly material is employed for the refracting prism.

Another very important function which the fixed-arm spectrometer can fulfil is that of a monochromatic illuminator. In many operations, both in spectroscopy and cognate work, it is essential to use light of one definite wave-length, as for example in interferometer or refractivity measurements. It is evident that for this purpose some form of fixed arm apparatus is necessary, in order to enable the wave-length of the light to be changed without alteration in the relative positions of the principal apparatus and the illuminator. Any fixed arm spectrometer can be converted into a monochromator by replacing the eyepiece by a slit placed in the focus of the telescope lens or mirror. For visible light the instrument shown in Fig. 51 is very well suited and is illustrated with the necessary modifications in Fig. 55.

This instrument is fully described by Tutton[1] for whom the first model was made. The two slits of the instrument are of the symmetrical type, which is very advisable since the optical centre of the ray does not shift when the width of the slits is varied. A ground glass screen can be mounted on an adjustable tubular fitting in front of the second slit in order to diffuse the emergent monochromatic light so that it may fill the field of any apparatus placed in front of it.

A somewhat similar instrument has been introduced for use as a monochromator for the ultra-violet. The apparatus is shown in Fig. 56 and, since a quartz prism must be used, the arrangement is somewhat different from that in the instrument previously described. The prism is a double one of the Cornu type (see p. 84) with refracting angle of 60°. The rays pass from the collimator lenses at minimum deviation through this prism to a plane mirror which reflects them into the telescope. By rotating the table carrying the prism and mirror, different rays pass into the telescope and are focussed on to the second slit. By this arrangement the rays emerging from the second slit have always traversed the prism at minimum deviation, the design being due to Wadsworth.[2] The tangent screw operating the prism table carries a divided drum from which the wave-length of the emergent ray can be directly read to about 10 Ångströms, the range of the instrument being from 7000 to 2000 Ångströms. The collimating and telescope lenses are not achromatic and consequently they are provided with adjustments for focussing, and in each case the necessary position can be read on a graduated scale which is shown on the collimator tube in the illustration.

It must be remembered that the accuracy of wave-length determination by visual reading cannot be compared with that obtained by photographic methods; in the latter case, photographs of the unknown spectrum and a standard spectrum are taken upon the same plate,

[1] *Crystallography*, Macmillan, London, 1911.
[2] *Phil. Mag.*, 38, 346 (1894).

superposed upon one another, or in juxtaposition, and the wave-lengths of the unknown lines are determined by measuring their positions on the photograph relatively to the known lines. A further disadvantage of the visual method lies in the fact that the ultra-violet region is not visible to the eye. It is true that an eyepiece can be constructed, which contains a layer of a fluorescing medium whereby ultra-violet lines can

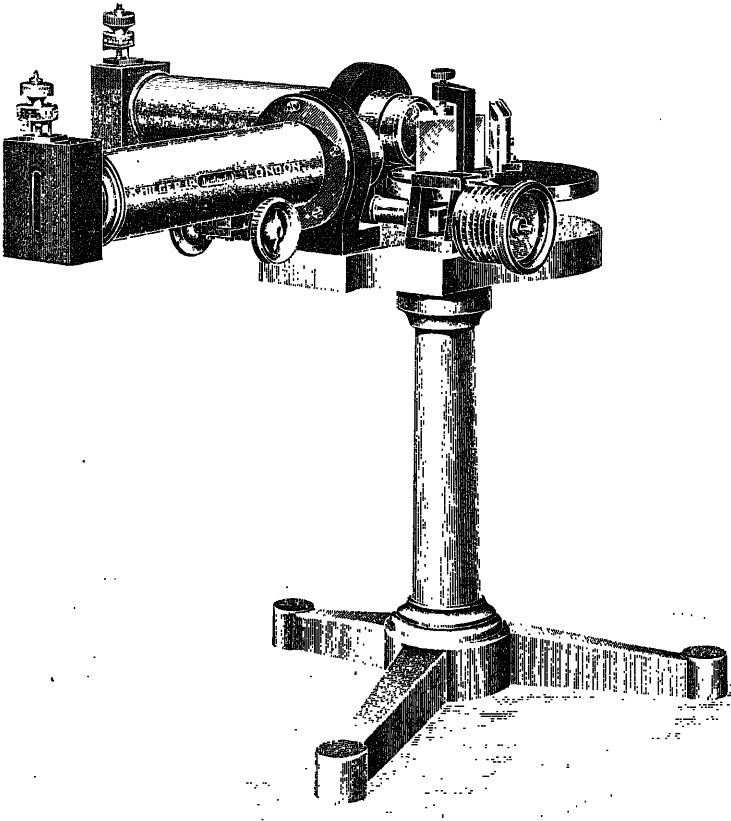


FIG. 56.

be visually detected, but these are of little use. In an apparatus for the photography of the spectrum a photographic plate is placed in lieu of the eyepiece in the focal plane of the telescope objective. It is obvious that the necessary apparatus may be very much simpler than in the case of a visual instrument, because there need be no moving parts. The name usually given to an apparatus designed for spectrum photography alone is a spectrograph.

It is, of course, possible to fit a photographic attachment to any of the spectroscopes described above; such an accessory is shown in Fig. 57. It consists of an oblong box A, to which is screwed the brass tube B; this tube B fits into the telescope tube in place of the eyepiece. The frame C is supported by two metal strips, which are shown at D; this frame C is pivoted so that it can be moved a little one way or the other around a vertical axis, this adjustment being necessary to correct for the possible want of achromatism of the telescope lens. The frame A is cut away, as shown, to allow for this movement, and leather bellows are fixed to A and C to keep out all extraneous light. The frame C is provided with grooves, just as in an ordinary camera, into which the dark slide fits. This little apparatus may be used to obtain photographs of small regions of the spectrum, small because the tube B has a small

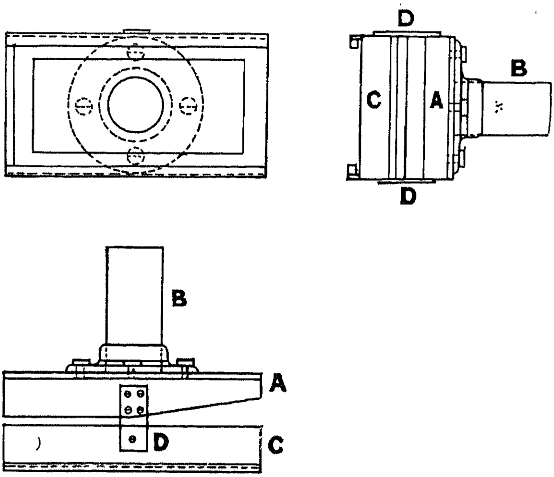


FIG. 57.

angular aperture, so that only a very short section of the spectrum can pass through at one time. It is very convenient to have vertical slides fixed upon the frame C to carry the dark slide. In this way if the latter is sufficiently broad several photographs can be [illegible] upon each plate; it is then preferable that the frame C have a horizontal rectangular aperture just sufficiently large to allow the free passage of the light to the plate. By altering the height of the plate-carrier in the vertical slides on C different portions of the plate can be exposed in turn, and in this way photographs of many spectra can be obtained on the same negative.

It is far better, however, if a spectrometer mounting be employed to remove the telescope tube altogether, and set in its place a wooden box, as shown in Fig. 58 in plan; the box is made to fit the spectrometer mounting in the same way as the original telescope. The telescope lens is at A, and is provided with a focussing arrangement B; the

rest explains itself. In this way none of the spectrum received by the telescope lens is cut off by any part of the apparatus. A spectrometer with the photographic attachment in position is shown in Fig. 59.

In Fig. 60 is shown a diagram of a mounting for a spectrograph which was set up at University College, London, and, perhaps, may be described on account of its extreme simplicity. The lenses are 2 inches in diameter, and of 5 feet focus, and there are two 60° prisms of glass. Both lenses are mounted in heavy brass cells screwed into brass tubes 2·5 inches in diameter and 6 inches long. The whole of the mounting of this apparatus is of wood, and is as simple as possible. It consists of two frames—one for the slit and collimator, and the other for the telescope lens and camera fittings. Each frame is composed of two pieces of 2-inch quartering, 6 feet long, bolted together with three iron bolts, one at each end and one in the middle. The pieces of quartering are separated by three small distance pieces, 1 inch thick, one at each bolt. The two pieces of quartering are shown at A, and the bolts at B, with the distance pieces C. It will be seen from the figure that a 1-inch slot is formed along the frames, and the tables carrying the lenses, etc., are provided with lugs, which fit into these slots. Underneath each frame is screwed the 1-inch board D, which serves to strengthen the whole, and guard against warping. Both frames are exactly similar, and form a very convenient basis for the mounting.

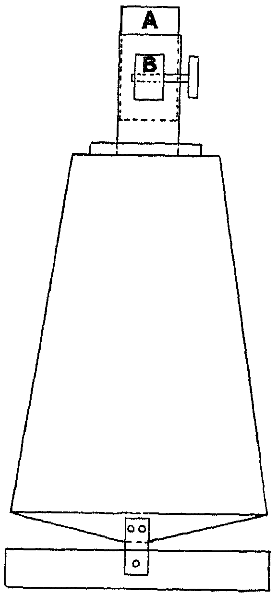


FIG. 58.

A diagram of the tables carrying the lenses and slit is shown at F; these are all of 1-inch wood, 5 inches square, and, as mentioned above, are firmly screwed to 1-inch lugs E, which fit into the slots. They can thus be put in any position, and, when all adjustments have been made, are securely fastened by screws into the pieces of quartering. The method of mounting the carrier tubes of the slit and two lenses, which is the same in each case, is as follows :—

The two side pieces G, G, which are screwed to the table running the whole length, are set at just sufficient distance apart to allow the carrier tubes to pass between them. The top H, slightly arched on its under side, can then be fastened down by screws into the side pieces, and serves to hold the carrier tubes firmly in their position.

The main prism table I, which is a board of 6 inches wide and $\frac{7}{8}$ inch thick, is screwed to the projecting end of the collimator frame at an angle of about 45°. The two prisms shown at K and L are mounted by a little Chatterton cement at each corner on two tables, $3\frac{1}{2}$ inches square

and $\frac{3}{16}$ inch, which are shown at M and N. These two tables are held by a single screw through their centres into the main table underneath, and are thus free to revolve. By this device, each prism can be rotated for the minimum deviation adjustment, and can be finally fixed in the required position by a small screw through the corner of its small table.

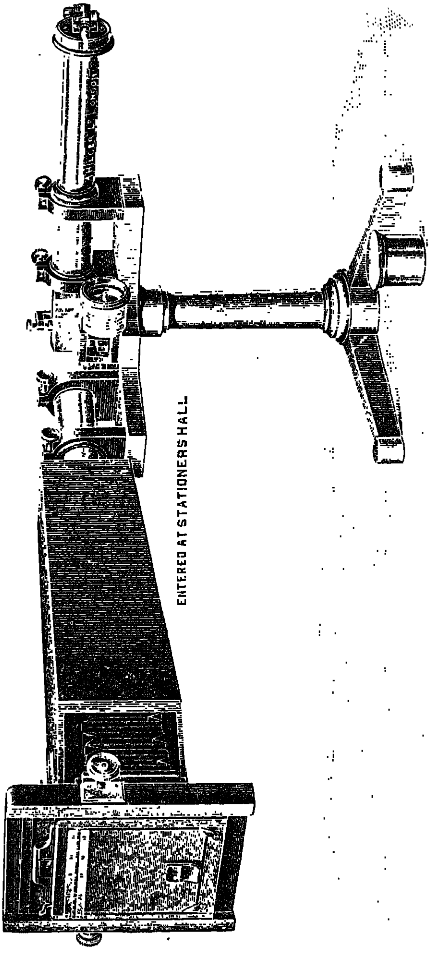


FIG. 59.

A small astronomical telescope is mounted to examine the spectrum reflected from the first surface of the second prism. The advantages of this are obvious for purposes of visual comparison, and for observing whether the slit is correctly illuminated.

The camera frame is fixed entirely separately from the collimator

frame. It is held by a single bolt about 1 inch from the end, not shown in the plan, which, passing through the supporting table, is clamped by a nut underneath. This bolt is placed vertically under the second prism, and thus the camera frame can be rotated, if necessary, for examination of different parts of the spectrum. The camera has, however, been made wide enough to take as much of the spectrum as is usually required for practical purposes; and, therefore, unless it be desired to examine the extreme blue part of the spectrum, this adjustment is not required.

The table which carries the dark slide differs slightly from the others;

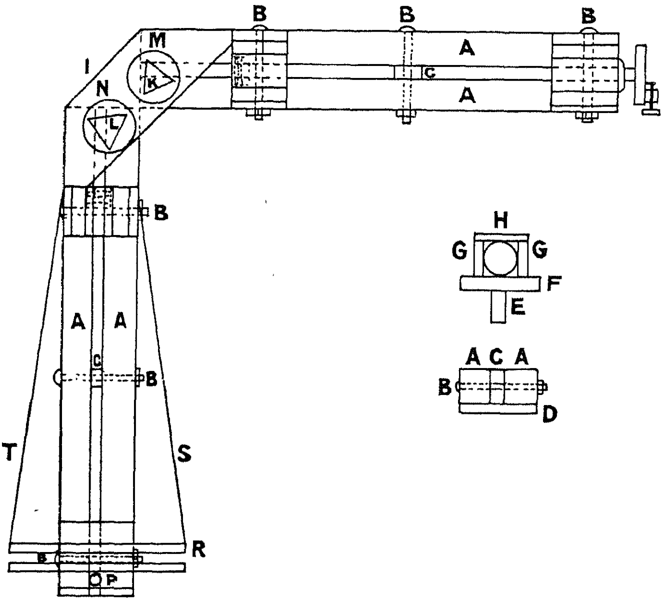


FIG. 6ↄ.

the chief difference lies in the fact that it is not fastened to its lug, but is held by a bolt, P, passing through its centre and the lug underneath. An angular adjustment is thus rendered possible, in addition to the motion parallel to the axis of the telescope lens. This adjustment, of course, is necessary in order to bring the photographic plate at the required angle to the axis of the lens, which is necessary for good focus. The position of the table can be fixed by a butterfly nut and large washer underneath the frame. A frame is erected vertically on the table, against which the dark slide is held by strong steel springs.

The length of the camera table and its frame is 12½ inches over all, with a centre aperture in the frame of 11 inches by 3½ inches.

The dark slide needs no special description. It carries a plate 11

inches by 3 inches, this length of plate being sufficient to photograph as much of the spectrum as can be focussed at the same time, with sufficient accuracy for good measurement.

When this apparatus was first set up, the spectrum photograph extended from wave-length 7000 to about 3800 Ångström units. The focus with this range was perfectly good, and though the prisms and lenses give a spectrum extending to 3100 Ångström units, the focus was not sufficiently good for the whole range, and, therefore, the ultra-violet portion was excluded, but could be obtained by swinging the camera frame round its bolt, as described above.

With regard to the method of covering the apparatus in order to protect it from daylight, this was done by means of two thicknesses of satteen, supported by light wooden laths, which were fastened to the upright side supports on the lens and slit tables. The satteen was nailed down on each side of the quartering, after being stretched tightly over the laths. A special arrangement, of course, was necessary in the case of the covering of the camera frame. The method adopted was as follows: a light frame, R, about 15 inches long by 6 inches high, was erected vertically on the camera frame about 4 inches in front of the camera table. Four laths, S and T, pass from the corners of this to the uprights on the table carrying the telescope lens. A double thickness of satteen was stretched over these and nailed underneath, along each side of the quartering. The space between this frame and the dark slide frame was covered loosely with satteen. The satteen was nailed all round the two frames, but was not stretched tightly between them, and a considerable latitude in the position of the dark slide table was thus obtained.

Any open spaces such as occurred at the corners of the mounting of the carrier tubes for the slit and two lenses were filled in with dark tailor's wool.

The prism part of the apparatus was covered with a loose velvet cloth, which was supported by a light wooden rail, carried by supports erected from the large prism table.

This arrangement has been found perfectly to exclude all light, the most rapid plates not being fogged, even though the room be illuminated with bright sunlight.

This apparatus has been thus described in detail in order to show how a perfectly serviceable mounting can be set up with the help of a carpenter at the cost of only a few shillings. In making a spectrograph, the essential point is that the slit, lenses, and prisms be of good quality; the mounting may very well be left to the ingenuity of the experimenter. A great number of designs have been brought forward, and any one of these may be adopted; but for ordinary laboratory work in photographing spectra it would appear that some such simple apparatus described above is as good as could be wished; in æsthetic appearance, perhaps, it may fail to please, but this is of small consequence in an apparatus destined for much use.

It is very evident that owing to the inability of the eye to detect light

vibrations of shorter wave-length than about $\lambda = 4000$, it is necessary to employ photographic methods when dealing with the ultra-violet regions of the spectrum. Although Schott & Co. have introduced a Uviol glass which is transparent to the ultra-violet rays as far down as $\lambda = 2800$, still an apparatus suitable for the photography of the whole ultra-violet must have its optical parts made of some material more transparent to these rays than glass. Quartz is by far the best substance, for calcite is not transparent to the extreme ultra-violet, and, moreover, the double refraction exhibited by it is a great drawback. In a prism spectrograph, therefore, intended for use in the ultra-violet, it is desirable that the prism at all events should be made of quartz. As regards the lenses, if fluorite only were obtainable at a reasonable price, the quartz-fluorite achromatic combination would be of great service. On the other hand, the quartz calcite combination suffers from the want of transparency to the extreme ultra-violet already mentioned. Generally speaking, if quartz lenses be used alone it will be found that the foci lie on a curve. Films must on this account be used so that they can be bent to the focal curve of the instrument. It is quite possible to construct a spectrograph with quartz optical parts and to cut a template which fits the focal curve. This template is mounted in the dark slide, and the photographic film is pressed up against the template by some suitable means.

It has been found possible, however, to cut the quartz prism and lenses in such a way that the focal curve is almost flat, although it lies at an acute angle (27°) with the axis of the telescope lens.

Instruments of this type are now to be obtained, and they rank amongst the most convenient forms for work in the ultra-violet region of the spectrum. They have the advantage of being absolutely transparent to all the ultra-violet rays, and at the same time giving excellent definition. Such an instrument is shown in Fig. 61. The dispersion system is a single Cornu prism of quartz and the quartz lenses have a focus of 8 inches. The dark slide takes quarter-plates and the whole spectrum from 8000 A. to 1850 A. is in good focus on a flat plate and is about 2·6 inches long. It is possible to construct an accurate scale of wave-lengths, [illegible] on glass for use with this instrument. Such a scale car [illegible] on to the spectrograms, whereby the wave-lengths of the lines can be read off with very fair accuracy.

A larger instrument of the same type is shown in Fig. 62. This apparatus has quartz lenses of 610 mm. focus and a Cornu prism with 41 mm. × 65 mm. face. The dark slide takes plates of 10 × 4 inches, and the spectrum from 8000 A. to 2100 A. is in perfect focus and about 8 inches long. A wave-length scale, which can be copied on each photographic plate, can be attached to this instrument. This scale is mounted on an arm operated by a lever outside the camera. When a spectrum photograph is taken the scale is turned away out of the path of the light, and when the scale is to be copied on to the photograph the lever handle is turned so that the scale is gently pressed against the photographic plate. Exposure is made by means of a very small electric

light bulb inside the camera, the whole of the rest of the plate being screened from the light.

A Littrow type of instrument may be mentioned, which is admirably adapted for very accurate work in the ultra-violet. The principle of the apparatus is as follows: The rays from the slit are reflected along the body of the instrument by a right-angled prism of quartz, collimated by a quartz lens and they then enter a half prism of quartz. The second face of the prism is coated with mercury tin amalgam and therefore the rays are reflected back through the prism. They pass once again through the lens and passing beneath the right-angle prism are brought

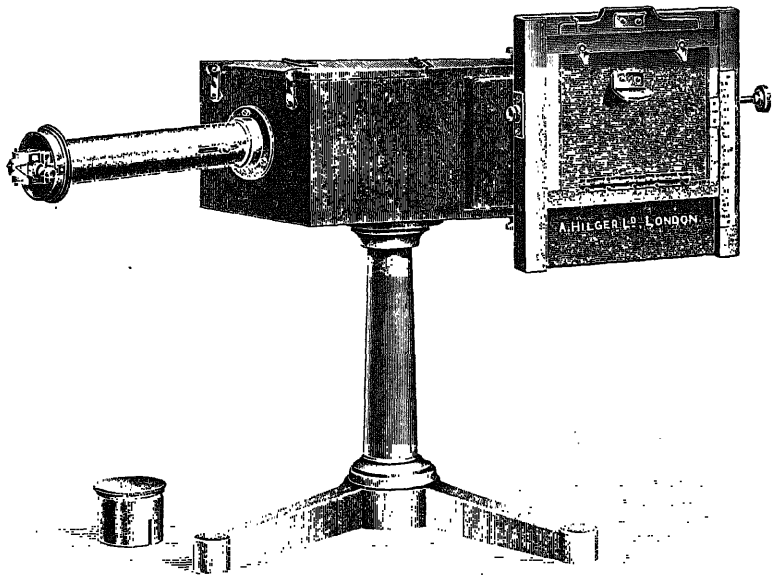


FIG. 61.

to a focus on the photographic plate. The lens has a clear aperture of 70 mm. and a focal length of 170 cm., whilst the refracting face of the prism is 98 mm. × 57 mm. The dark slide takes plates of 10 × 4 inches and the whole spectrum from 8000 A. to 2100 A. is taken in three separate exposures. There are three adjustments in the apparatus, the position of the lens, the position of the prism, and its angular rotation.

Each of these has its own graduated scale and thus the necessary adjustments for the photography of any region of the spectrum can be determined and recovered at any time. An external view of this spectrograph is shown in Fig. 63.

For many purposes it is not necessary to use a spectrograph which transmits the whole of the ultra-violet and in particular is this the case in metallurgical work, such as the spectrographic analysis of steels. The

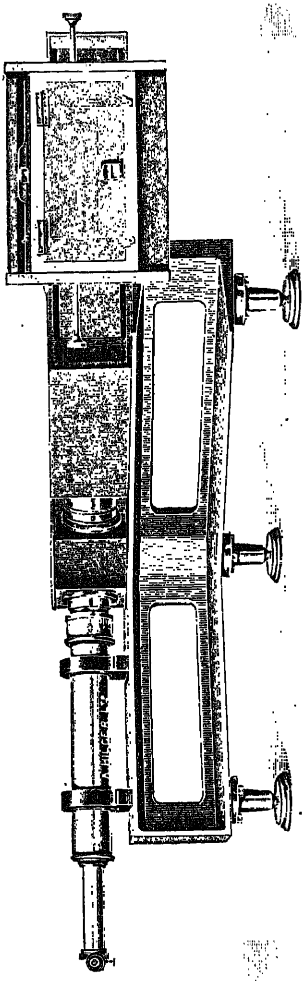


Fig. 62.

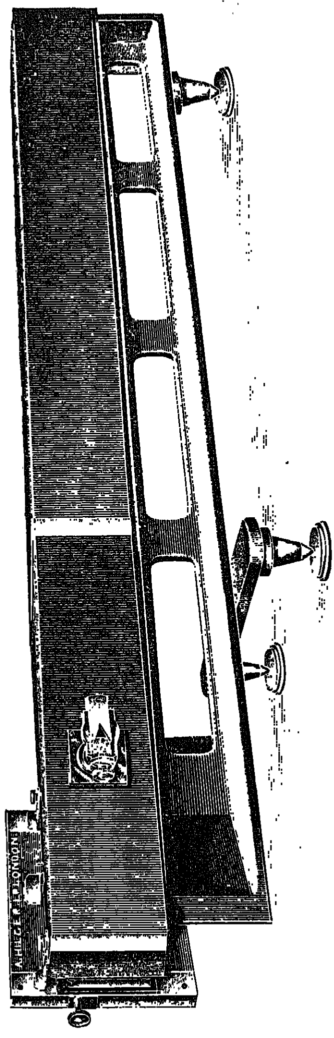


Fig. 63.

quartz lenses and prism can then be replaced by the Uviol glass of Schott & Co. with the result that a greater dispersion can be obtained without much increase in price. In quantitative spectroscopic analysis, depending on the "persistence" of spectrum lines, it is found that the

great majority of the lines used in this method have a larger wave-length than 3170 A., which is the effective limit of a spectrograph with Uviol glass optical parts. Such an instrument is shown in Fig. 64 and is similar in construction to that illustrated in Fig. 62. This instrument has two 60° prisms of Uviol glass and the lenses give a perfectly flat field,

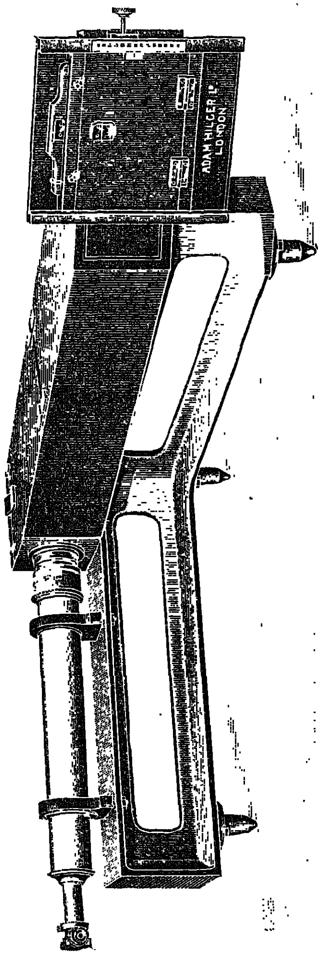


FIG. 64.

the spectrum from 7000 A. to 3170 A. being photographed on a half plate ($6\frac{1}{2} \times 4\frac{3}{4}$ inches). A [illegible] scale similar to that described for Fig. 62 can also be [illegible] spectrograph. The lenses are constructed of pairs of glasses similar to ZK5 and PK1 or BK5 (see p. 76) and the smaller transparency of the first to the ultra-violet

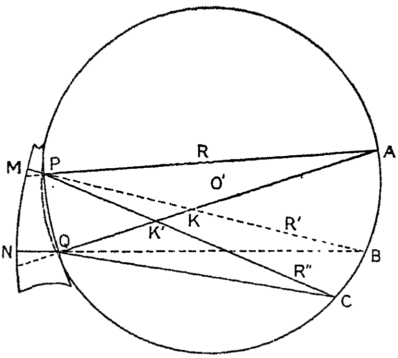


FIG. 65.

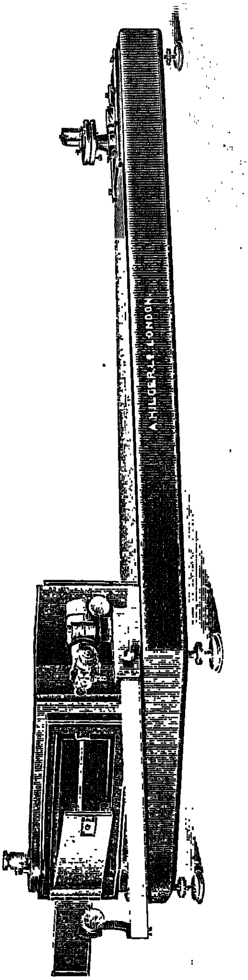


FIG. 66.

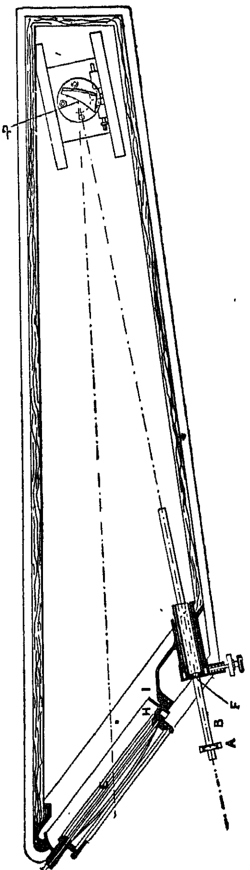


FIG. 67.

accounts for the fact that with this instrument the spectrum does not extend beyond 3170 A.

A novel form of quartz spectrograph has been devised by Féry,[1] who makes use of a prism with curved faces and thereby eliminates all lenses. The theory of the instrument is exceedingly simple, as may be seen on reference to Fig. 65, where R is the radius of curvature of the front face of the prism MPQN. Then the lines CP, CQ make equal angles i with the normals AP, AQ. The slit is placed at C, and any bundle of monochromatic rays from C falling on the front prism face will be refracted, making the angles r with the normals. If the paths of these rays be prolonged they will meet at B, which is the centre of curvature of the second curved face of the prism, MN. This second surface is coated with mercury tin amalgam and therefore the rays will be returned to an exact focus on the slit. It is easy to see that the points ABCQP all lie on a circle, so that the two centres of curvature, the slit and the spectrum, lie on the same circle. In actual practice the slit is moved round the circle a little so as to increase the incidence angle i, with the result that the spectrum will be brought to a focus on the circle a short distance from the slit. In addition to the elimination of all lenses, there is no trouble caused by the rotatory power of the quartz since the light traverses the prism twice in opposite directions. The complete instrument is shown in Figs. 66 and 67. In Fig. 67 P is the prism, F the slit, E the curved photographic plate, and A a condensing lens. A further point in connection with this apparatus is that a certain amount of astigmatism occurs, as in the case of Rowland's concave grating (see p. 165). A comparison of two spectra by draw slides over the slit is therefore not possible, but is carried out by means of a movable screen, with a rectangular opening, which is placed immediately in front of the photographic plate.

A very useful addition to any spectrograph is to have the dark slide which carries the photographic plate working in vertical grooves. In this way by moving the plate up or down in its grooves a number of photographs may be taken upon the same plate. A rack and pinion arrangement should be attached so as to allow the dark slide to be brought to any desired position, and it is also well to have a scale marked on the frame carrying the dark slide, so that the position of the plate may at any time be read. It is necessary, if a great number of spectra are to be photographed upon one plate, to limit the width of each spectrum sufficiently to allow of this without the successive photographs overlapping, This may be done either by using only a very short slit or by having a screen with a narrow rectangular opening placed just in front of the photographic plate. The arrangement is shown in most of the instruments illustrated above.

[1] *Journ. de Physique*, 9, 762 (1910); and *Astrophys. Journ.*, 34, 79 (1911).

CHAPTER V.

THE PRISM SPECTROSCOPE IN PRACTICE.

The Adjustment of the Prism Spectroscope.—For the complete adjustment of a prism spectroscope it is necessary that the following conditions be satisfied :—

(1) That the collimating lens direct a beam of parallel light upon the first prism face.

(2) That the optic axes of the collimator and telescope pass through the same principal plane of the prism whatever may be the position of the telescope.

(3) That the opening of the slit be parallel to the refracting edge of the prism.

The methods of adjustment of the apparatus, so that these three conditions may be satisfied, may be described in detail for the case of an ordinary spectrometer with one prism, similar methods being applicable to the more complex instruments. First of all, the telescope of the instrument should be focussed for parallel rays ; the eyepiece is first adjusted so that the cross-threads are in good focus, and then the telescope is directed towards some very distant object, such as a church spire or flagstaff, and the whole eyepiece moved in or out until the object is seen to be well defined. This focus will be found to be sufficiently near to that actually necessary for objects at an infinite distance, that is to say, for parallel rays. The slit of the instrument is then illuminated by some convenient source of light, such as an ordinary gas-flame, and the telescope and collimator brought into line with one another so that the image of the slit can be seen direct without the interposition of the prism. The collimator is then focussed until a perfectly sharp image of the slit is seen; the collimator will then be approximately in correct adjustment. The centre of the image of the slit should be seen in the centre of the field of view in the telescopic eyepiece, and then the axes of the telescope and collimator will form portions of the same straight line.

A convenient way to test this adjustment is to cover the slit with a piece of cardboard having a small hole cut in it a millimeter or so in diameter.[1] In this way only the central portion of the slit is exposed to the illumination, and this should be seen in the centre of the field of view in the telescope ; if it appears above or below the centre the colli-

[1] Very often the slit is provided with a wedge-shaped diaphragm which works in grooves outside the jaws (see Fig. 21). This is very convenient in the above adjustment.

mator and telescope are carefully adjusted until they are properly level. Care must also be taken to see that the slit opening is truly vertical. The prism is then put in place and levelled so that the refracting edge is vertical and parallel to the slit.

One of the following methods may be used for the more accurate adjustment of the collimator focus for parallel rays. First, Schuster's method [1]—the prism is set in the position of minimum deviation, and the telescope turned so that the image of the D line or some other convenient ray is seen. The telescope is then turned a little to one side of the image; it is evident that there are now two positions of the prism, one on each side of that of minimum deviation, which will bring the image of the line again into view in the centre of the field of the telescope. The prism is turned to these two positions in succession, and the line observed in each case; if the line appears in perfectly good focus at each time, then the telescope and collimator are both accurately adjusted for parallel rays. If, however, as is more probable, the focus of the line appears better at one time than at the other, the following procedure is adopted. The prism is first turned to the one position, and then the collimator is focussed until the line is seen perfectly sharp; after turning the prism to the other position the telescope is focussed to produce the best definition. After one or two repetitions it will be found that the condition will be obtained that the line remains in perfect focus whichever way the prism is turned. This corresponds to perfect adjustment of both the collimator and telescope for parallel rays.

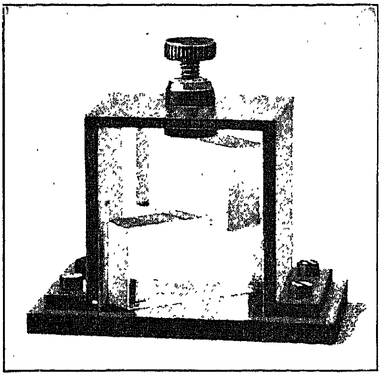


FIG. 68.

The second method is that devised by Lippmann,[2] who employs two strips of plane-parallel glass plate, which are set one above the other and at right angles to one another. This apparatus is set in the path of the rays from the collimator; if these rays be truly parallel no effect will be produced, but if they be convergent or divergent, the upper and lower halves of the image of the slit will appear relatively displaced. The apparatus is shown in Fig. 68.

In an ordinary spectrometer with achromatic glass lenses, when the collimator has been adjusted for giving parallel rays of one wave-length, this adjustment will be suitable for all the rays of the spectrum. It must be remembered, however, that the eyepiece is not achromatic in every sense of the word; as was explained in Chapter III., the eyepiece is so adjusted that the different coloured images all have the same apparent

[1] *Phil. Mag.*, **7**, 95 (1879). [2] *Comptes Rendus*, **129**, 569 (1899).

size. As these are still distributed along the axis, a different focus of the telescope is required for rays of different wave-lengths. When non-achromatised lenses are employed, such as simple lenses of quartz, if the focus of the collimator be found for rays of known wave-length, the focus for any other ray may be found by simple calculation from the ordinary formulæ of lenses, and the relative position of slit and collimating lens altered accordingly. It is very convenient for this purpose to have the focussing tube of the collimator graduated in millimetres in order to allow of a definite change in the focus being made, such as will be required in moving from one part of the spectrum to another.

In the adjustment of prism apparatus for the photography of the spectrum, we have, in addition to the previous adjustments, the focussing of the photographic plate in order to obtain the best definition. Generally speaking, in apparatus in which considerable portions of the spectrum are photographed upon one plate, the collimator is adjusted for parallelism and the prisms set at minimum deviation for the mean rays of the region photographed. Better definition of the photographed lines is more likely to be obtained in this way. There are two separate adjustments to be attended to with respect to the photographic plate, viz., the distance of the plate from the camera lens, and its angle to the axis of the lens; these adjustments resolve themselves into a series of trials by error. In the photographic apparatus described in the last chapter the camera back was shown to be mounted in such a way that it can be rotated round a central vertical axis; this is necessary in order to obtain the required tilt of the plate. A preliminary focussing of the plate may readily be obtained by the use of a ground-glass screen as is customary in ordinary photography; a photograph of the spectrum is then taken, and if the definition is not satisfactory the camera back is moved to or from the lens and a second photograph taken. This is repeated until the lines in the central portion of the plate are in perfect focus. It only remains now to alter the tilt of the plate until the whole spectrum, or as much of it as possible, is in focus.

Whilst in the case of glass, quartz-fluorite, or quartz-calcite achromats it is possible to obtain a flat field, and therefore to use glass photographic plates, this is not generally secured with uncorrected lenses, especially if large portions of the spectrum are to be photographed upon the same plate. Under these circumstances the focus of the objective lies upon a curve, and it becomes necessary to use films. A frame cut to agree with the focal curve is fixed in the plate-holder, and the film is held up against this frame during an exposure. Such a plate-holder is shown in the Féry spectrograph illustrated in Fig. 66. As was described in the preceding chapter quartz spectrographs are now made which give the whole spectrum from 8000 A. to 2100 A. in perfect focus on a flat field. These instruments are sent out by the makers in perfect adjustment, or, as in the case of the large Littrow instrument shown in Fig. 63, with the necessary adjustments clearly stated for each section of the spectrum.

In the final testing of the focus it is advisable to use a source of light the spectrum of which is known to consist of fine, sharply defined lines.

Metallic spectra very often contain some lines which are diffused on one or both sides; such lines may be neglected in the adjustment of the apparatus for the best definition. One of the most satisfactory sources of illumination for this purpose is a vacuum tube containing carbon dioxide or air, as the spectrum given by such a tube when the electric current passes through it is one of bands of extremely fine lines. For use in the ultra-violet a quartz vacuum tube must be used or glass tube with a quartz window viewed end-on. See Volume II, Chapter IV.

For the purpose of improving the illumination it is customary to focus an image of the source upon the slit by means of a condensing lens; in this way, unless the source is very large or very near the slit, considerably more light is obtained. An advantage is also gained in the case of flame spectra, in that the slit is not subjected to any possible spluttering or splashing of the salt in the flame.

The Methods of Wave-length Determination with the Prism Spectroscope.—In the case of the prism spectroscope, almost all methods of determination of the wave-lengths of spectrum lines are carried out by processes of comparison between them and the lines of other spectra, the wave-lengths of which have already been accurately determined; that is to say, the position of the unknown lines in the spectrum are measured relatively to the positions of certain well-known lines, and the wave-lengths are obtained by interpolation. In the case of the visible portion of the spectrum this may be done by means of eye observations if great accuracy be not required, but, generally speaking, photographic methods are to be recommended owing to their greater reliability.

For visual work some sort of scale must be employed, on which the positions of the lines are read; this may be a scale photographed upon glass, which, by reflection from the last prism face, is viewed at the same time as the spectrum, and is so adjusted as to appear above or below it, and adjacent to its edge. This was used by Bunsen and Kirchhoff, and the position of the lines may be readily read upon it, but only quite roughly, so that the method can hardly be recommended at the present time. It is important to note that such a photographed scale very easily shifts its position relatively to the spectrum; it is necessary therefore, that the scale be provided with some form of adjustment, by means of which its position can be altered; when using the instrument at any time, care should be taken that the scale is correctly placed, which may quite readily be realised by arranging that some line, such as the D line, be brought to the same reading; this must always be carried out before any series of measurements are made.

Far better than the method of the photographed scale is the method of measuring the deviations of the line, which may be carried to a greater pitch of accuracy. The apparatus used for this purpose, known as the spectrometer, has already been sufficiently described, and it only remains to show how the method is put into practice. If possible, it is better always to work with the prism in the position of minimum deviation for every ray examined; this is a necessity in the case of calcite prisms, and

is to be preferred with those of other media. In actual observations the fixed pointer or spider web in the eyepiece is first of all focussed, and then, after focussing the image of the slit directly without the intervention of the prism, the position of the telescope is read upon the divided circle; the telescope is then moved until the pointer is adjusted exactly upon a spectrum line, when the position is again read upon the divided circle. Consecutive readings should show the smallest possible or no difference amongst themselves.

In order to find the wave-length of an unknown line from such visual methods one may use the method of graphical interpolation or an interpolation formula such as Hartmann's, which was mentioned on p. 59. The use of this formula is very simple, but will be understood more easily when applied to a photographed spectrum, and therefore it will be exemplified below (see p. 141). The method of graphical interpolation consists in drawing the dispersion curve of the spectroscope; that is to say, the curve expressing the relation between wave-length and the deviation produced. In order to obtain this curve, a number of well-known lines in different parts of the spectrum are chosen, and their deviations measured as accurately as possible. These numbers, together with the wave-lengths or wave numbers of the lines, are then plotted on squared paper, and a curve drawn through the points obtained; this curve must, of course, be perfectly smooth, without any sudden changes of direction, and it is the more accurate the greater the number of lines measured for the purpose. When this curve has once been drawn for an instrument, the determination of the wave-length of an unknown line becomes very simple; it is only necessary to measure its deviation, when the wave-length can be read directly off from the curve.

The choice of lines must be left to the discretion of the experimenter, but it must be remembered that only sharp and well-defined lines should be taken. The most satisfactory in this respect are the lines given by gases under reduced pressure, and those given by hydrogen and helium will probably be found to be sufficient for ordinary purposes. Collie[1] has pointed out that if the helium and hydrogen be mixed with mercury vapour, certain lines in the mercury spectrum will appear very strongly accentuated. He recommends the use of such a vacuum tube for the calibration of a spectrometer. The wave-lengths of the lines in this spectrum are as follows:—

Helium,	red,	7281·35	Ångströms.	Helium,	green,	4921·93	Ångströms.
Helium,	red,	7065·19	,,	Hydrogen,	blue,	4861·39	,,
Helium,	red,	6678·15	,,	Helium,	blue,	4713·14	,,
Hydrogen,	red,	6562·82	,,	Helium,	violet,	4471·48	,,
Mercury,	orange,	6152·3	,,	Helium,	violet,	4437·55	,,
Helium,	yellow,	5875·62	,,	Helium,	violet,	4387·93	,,
Mercury,	yellow,	5790·66	,,	Mercury,	violet,	4358·34	,,
Mercury,	yellow,	5769·90	,,	Hydrogen,	violet,	4340·37	,,
Mercury,	green,	5460·74	,,	Helium,	violet,	4120·81	,,
Helium,	green,	5047·74	,,	Hydrogen,	violet,	4101·85	,,
Helium,	green,	5015·68	,,	Helium,	violet,	4026·19	,,

[1] *Proc. Roy. Soc.*, 71, 25 (1902).

There are in this list twenty-two lines which are fairly equally distributed over the spectrum, and should prove sufficiently numerous for the purposes of the calibration curve of an ordinary laboratory instrument. If, however, more lines are required in order to render the curve more accurate, these may readily be found in the spark spectra of cadmium and of copper, and some other metals. From the helium, hydrogen, and mercury lines, it is quite possible to draw a calibration curve which is almost correct throughout its whole length; when once this curve has been drawn it is a simple matter to read the deviations of more lines which may afterwards be put upon the curve. When the spectra of metals are employed it is often difficult to recognise any lines amongst the great number which are visible; but by means of the approximate calibration curve, the wave-lengths may be found with sufficient approximation to recognise them in a list of the lines of the element. The true wave-lengths may then be used to correct the curve. The principal lines in the visible regions of the spark spectra of copper and cadmium may be given here:—

Cadmium.	Copper.	Cadmium.	Copper.
6438·47	5782·16	4216·9	4911·0
5379·0	5700·25	4126·9	4704·8
5338·3	5295·55	4094·8	4651·15
5085·82	5218·20	4057·6	4587·01
4799·91	5153·26	3988·3	4539·7
4678·15	5105·58		4275·3
4415·68	4932·7		

It will be found that if, instead of the wave-lengths, the wave numbers of the lines be used, the shape of the curve will be flatter, and thus it becomes rather easier to draw. By the wave number is meant the number of waves contained in one centimetre in vacuo, that is to say, the reciprocal of the wave-length reduced to vacuum. In order to reduce the wave-length of any line measured in air to its real value in vacuo it is necessary to multiply by the refractive index of air for light of the particular wave-length. The most accurate values of the refractivities of air have been obtained by Meggers and Peters,[1] whose measurements at 15° are given by the following formula:—

$$(n - 1) \times 10^7 = 2726{\cdot}43 + \frac{12{\cdot}288}{\lambda^2 \times 10^{-8}} + \frac{0{\cdot}3555}{\lambda^4 \times 10^{-16}},$$

λ being expressed in Ångströms. As was explained on page 41, it is simplest to add a small number, $\lambda(n - 1)$, to the wave-length measured in air in order to reduce it to vacuum. The following values of the refractivities and the corrections are quoted from Meggers and Peters' paper:—

[1] Scientific Papers of the Bureau of Standards, No. 327, Washington, 1918, *Astrophys. Journ.*, 50, 56 (1919).

λ.	$(n-1)10^7$.	$(n\lambda - \lambda.)$	λ.	$(n-1)10^7$.	$(n\lambda - \lambda.)$
10,000	2739·07	2·7391			
9950	2739·20	2·7255	7700	2748·17	2·1161
9900	2739·34	2·7119	7650	2748·47	2·1026
9850	2739·47	2·6984	7600	2748·77	2·0891
9800	2739·61	2·6848	7550	2749·08	2·0756
9750	2739·75	2·6713	7500	2749·40	2·0620
9700	2739·89	2·6577	7450	2749·72	2·0485
9650	2740·04	2·6441	7400	2750·06	2·0350
9600	2740·18	2·6306	7350	2750·39	2·0215
9550	2740·33	2·6170	7300	2750·74	2·0080
9500	2740·48	2·6035	7250	2751·10	1·9945
9450	2740·64	2·5899	7200	2751·46	1·9811
9400	2740·79	2·5763	7150	2751·83	1·9676
9350	2740·95	2·5628	7100	2752·21	1·9541
9300	2741·11	2·5492	7050	2752·59	1·9406
9250	2741·28	2·5357	7000	2752·99	1·9271
9200	2741·44	2·5221	6950	2753·39	1·9136
9150	2741·61	2·5086	6900	2753·81	1·9001
9100	2741·79	2·4950	6850	2754·23	1·8866
9050	2741·96	2·4815	6800	2754·67	1·8732
9000	2742·14	2·4679	6750	2755·11	1·8597
8950	2742·32	2·4544	6700	2755·57	1·8462
8900	2742·51	2·4408	6650	2756·04	1·8328
8850	2742·70	2·4273	6600	2756·51	1·8193
8800	2742·89	2·4137	6550	2757·00	1·8058
8750	2743·09	2·4002	6500	2757·51	1·7924
8700	2743·29	2·3867	6450	2758·02	1·7789
8650	2743·49	2·3731	6400	2758·55	1·7655
8600	2743·69	2·3596	6350	2759·09	1·7520
8550	2743·90	2·3460	6300	2759·65	1·7386
8500	2744·12	2·3325	6250	2760·22	1·7251
8450	2744·34	2·3190	6200	2760·80	1·7117
8400	2744·56	2·3054	6150	2761·40	1·6983
8350	2744·79	2·2919	6100	2762·02	1·6848
8300	2745·02	2·2784	6050	2762·65	1·6714
8250	2745·25	2·2648	6000	2763·31	1·6580
8200	2745·49	2·2513	5950	2763·98	1·6446
8150	2745·74	2·2378	5900	2764·66	1·6311
8100	2745·99	2·2243	5850	2765·37	1·6177
8050	2746·24	2·2107	5800	2766·10	1·6043
8000	2746·50	2·1972	5750	2766·85	1·5909
7950	2746·76	2·1837	5700	2767·62	1·5775
7900	2747·03	2·1702	5650	2768·41	1·5642
7850	2747·31	2·1566	5600	2769·23	1·5508
7800	2747·59	2·1431	5550	2770·07	1·5374
7750	2747·88	2·1296	5500	2770·94	1·5240

λ.	$(n-1).0^7$.	$(n\lambda - \lambda.)$	λ.	$(n-1)10^7$.	$(n\lambda - \lambda.)$
5450	2771·83	1·5106	3700	2835·16	1·0490
5400	2772·75	1·4973	3650	2838·69	1·0361
5350	2773·70	1·4839	3600	2842·41	1·0233
5300	2774·68	1·4706	3550	2846·32	1·0104
5250	2775·69	1·4572	3500	2850·43	0·9977
5200	2776·74	1·4439	3450	2854·76	0·9849
5150	2777·81	1·4306	3400	2859·33	0·9722
5100	2778·93	1·4173	3350	2864·15	0·9595
5050	2780·08	1·4039	3300	2869·24	0 9469
5000	2781·27	1·3906	3250	2874·63	0·9343
4950	2782·50	1·3773	3200	2880·33	0·9217
4900	2783·78	1·3640	3150	2886·38	0·9092
4850	2785·09	1·3508	3100	2892·79	0·8968
4800	2786·46	1·3375	3050	2899·60	0·8844
4750	2787·88	1·3242	3000	2906·85	0·8721
4700	2789·34	1·3110	2950	2914·57	0·8598
4650	2790·86	1·2978	2900	2922·80	0 8476
4600	2792·44	1·2845	2850	2931·60	0·8355
4550	2794·08	1·2713	2800	2941·00	0·8235
4500	2795·78	1·2581	2750	2951·08	0·8115
4450	2797·55	1·2449	2700	2961·88	0·7997
4400	2799·39	1 2317	2650	2973·50	0·7880
4350	2801·30	1·2186	2600	2986·00	0·7764
4300	2803·29	1·2054	2550	2999·48	0·7649
4250	2805·36	1·1923	2500	3014·05	0·7535
4200	2807·51	1·1792	2450	3029·81	0·7423
4150	2809·76	1·1661	2400	3046·91	0·7313
4100	2812·11	1·1530	2350	3065·50	0·7204
4050	2814·56	1·1399	2300	3085·75	0·7097
4000	2817·12	1·1268	2250	3107·67	0·6993
3950	2819·79	1·1138	2200	3132·07	0·6891
3900	2822·59	1·1008	2150	3158·63	0·6791
3850	2825·51	1·0878	2100	3187·86	0·6695
3800	2828·58	1·0749	2050	3220·12	0·6601
3750	2831·79	1·0619	2000	3255·82	0·6512

In Fig. 69 are shown two calibration curves of a spectrometer, one, ., being drawn with the wave-lengths of the spectrum lines, and the ther, B, with the wave-numbers; the same lines are used in each ase. As can be seen from the curves, the angular deviations of the nes are expressed on the abscissæ; on the ordinates are expressed the ave-lengths in one case, and the wave-numbers in the other case.

The determination of wave-lengths in this way by visual observation an be quickly carried out, and serves excellently well for the identifica- on of lines in a qualitative way; it is possible, of course, to use an strument of high dispersion and resolving power, and by its means raw a dispersion curve on a large scale, from which the wave-lengths

of unknown lines may be determined with considerable accuracy. For the drawing of such an extended curve a great number of points must be read so as to obtain the required accuracy, but it is doubtful whether this is worth the extra trouble and expense involved. It is far preferable to have recourse to photographic methods of comparison, which are able to give much more accurate results with much less costly apparatus.

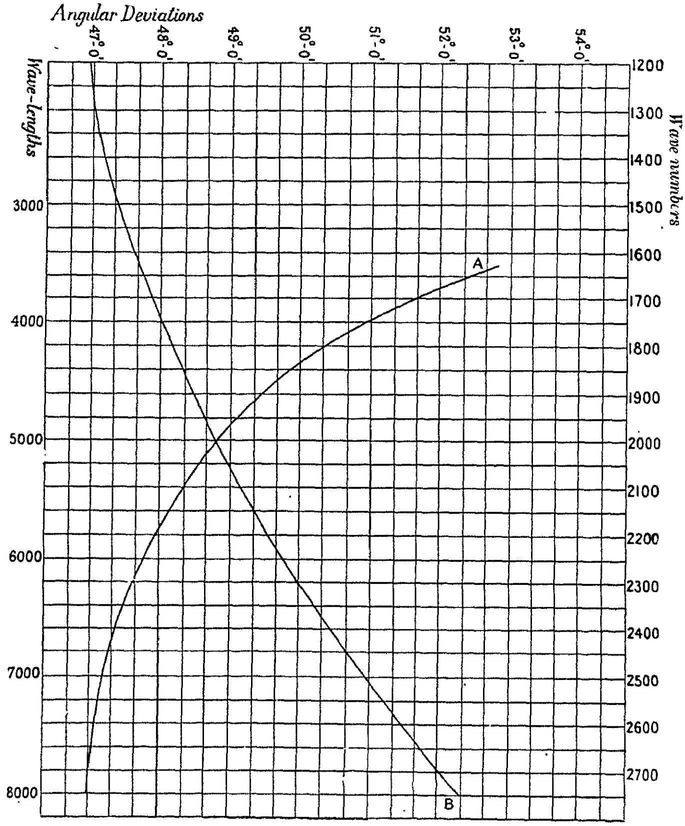


FIG. 69.

It will, of course, be remembered that the use of a direct reading wave-length spectrometer, such as that shown in Fig. 51, entirely eliminates the necessity for graphical interpolation. The method of measurement with this type of instrument is exceedingly simple. After the apparatus has been correctly levelled the reading on the scroll of the drum should be the correct wave-length of the spectrum line on which the spider web in the eyepiece has been set. If, however, this

is found not to be the case, the prism is then not correctly oriented and its position must be changed. As a rule, it is only necessary to turn the prism a little on its table. The slit is illuminated with the rays from some convenient source, such as a hydrogen vacuum tube, and the scroll is adjusted to give the correct reading for one of the spectrum lines. The screw holding the prism in position is then loosened and the prism turned a little in one or other direction until the spectrum line coincides with the image of the spider web. When this has been secured, the screw is gently turned until the prism is just held securely in position, care being taken not to fix it too tightly so as to guard against any strain being set up. After this has been done, if the spectrum line is not quite in the correct position, the spider web may be moved a little by means of the adjusting screw in the eyepiece so as to obtain as perfect a setting as possible. The instrument will then be in correct adjustment and readings of wave-lengths can be made correct to within about 2A.

The photographic method consists in obtaining, with the same instrument, photographs of the unknown spectrum, and a standard spectrum upon the same plate, when the unknown wave-lengths are obtained by interpolation between the wave-lengths of the lines in the standard spectrum. The method is quite similar to the graphical interpolation described above, because the photograph gives a permanent record of the deviations suffered by the various lines. The standard spectrum is so chosen as to contain a great number of lines, and there is no need to draw the dispersion curve, since the change in dispersion over a small range of the spectrum is not large enough to introduce sensible errors in a simple linear interpolation, unless very great accuracy is demanded. In work of the highest accuracy measurements are made of a considerable length of the photographed spectrum and a curve of errors drawn as explained below.

In this photographic comparison of spectra care should be taken that the two spectra be quite contiguous to one another, still better, that they should overlap one another a little, in order to render the relative measurement of the two photographs more accurate.

It will be found on comparing two spectra that unless the rays from the two sources of light fall upon the slit at the same angle, the two spectra will be slightly displaced relatively to one another upon the photographic plate, owing to the fact that different parts of the collimating lens are used in each case.[1] In accurate work, therefore, it is necessary to guard against this by ensuring that the two sources of light are placed in identical positions. This may be readily secured by the use of a lens for focussing an image of the source upon the slit. An image of the light source chosen as the standard, *e.g.* the arc between

[1] For this reason the right-angled comparison prism is useless for the accurate comparison of spectra; this accessory is to be recommended only for rough visual comparisons. For more accurate work, when two spectra are photographically compared, it is necessary to photograph the two sources in succession through adjacent portions of the slit as described in the text.

iron poles, is focussed upon a portion of the slit, care being taken that the arc, the slit, and the centre of the collimating lens lie on the same straight line. When the spectrum of this source has been photographed, the arc is removed and the second light source set in its place, so that, without moving the condensing lens, the image of the source is focussed upon the slit a little above or below the place upon which the image of the arc was previously thrown. The spectrum of this light is now photographed, and it will then be found that the two spectra upon the plate are quite correctly placed in relation to one another. It is hardly necessary to point out that the slide of the camera plate-carrier should not be shut after it has once been opened until the two photographs have been obtained, as otherwise the plate is certain to be moved; it is necessary to cover the slit with a piece of black paper, which is removed during the exposing of the plate; or, better, the draw slides or perforated diaphragm described upon p. 46 may be used, and will be found to be extremely useful for the purpose. When a photograph of the standard and the unknown spectrum has been obtained in this way, it only remains to measure the relative positions of the known and unknown lines from which the wave-lengths of the latter may be computed.

A few words may be said about the choice of the standards of comparison. The most satisfactory of these is the spectrum of the iron arc, although its use may at first entail a little trouble owing to its complexity. It has, however, the great advantage in that the majority of secondary and tertiary standards on the international system are to be found therein. The initial difficulty of recognising the lines can readily be surmounted by comparing a photograph of the spectrum with a map as explained below. As was stated in the historical introduction, the secondary standards have not as yet been carried beyond 3370 I.A., and until standards of smaller wave-length have been definitely adopted the wave-lengths in the iron spectrum, as given in opposite page, may be used with every confidence.[1]

The International Union in 1913[2] laid down the following conditions for using the iron arc:

1. The length of the arc to be 6 mm.

2. For wave-lengths greater than 4000 A. the current to be 6 amps., and for those less than 4000 A. to be 4 amps. or less where possible.

3. Direct current to be used with a voltage of 220 volts, the positive pole being above the negative, and the diameter of the electrodes being 7 mm.

4. As light source an axial portion to be used, about 2 mm. long, out of the middle of the arc.

5. Only the lines of groups *a*, *b*, *c*, and *d* of the Mount Wilson classification to be used.[3] The definition of the lines of groups *c* (class 5)

[1] *Trans. International Astron. Union I*, 39 (1922), Imperial College Bookstall, London.

[2] *Trans. International Union for Co-op. in Solar Research*, 4, 59 (1913). Manchester University Press.

[3] Gale and Adams, *Astrophys. Journ.*, 35, 10 (1912).

and *d* is better when the slit is at right angles to and in the middle of the arc, or when the direction of the current is changed a number of times during the exposure.

In 1922 the International Astronomical Union agreed that the Pfund arc (see Volume II., Chapter IV.) be used and that the current be 5 amps. or less at 110 to 250 volts. The upper pole to be an iron rod 6 to 7 mm. in diameter and an iron oxide bead to be the lower pole. The length of the arc to be 12 to 15 mm. and the radiation to be used from a horizontal central zone not exceeding 1 to 1·5 mm. in width.

Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Intensity.
3337·671	4	3083·745	4	2858·898	4	2598·380	7
3325·468	4	3078·436	3	2851·798	8	2584·544	4
3323·741	4	3068·180	4	2848·714	4	2566·921	4
3317·126	4	3055·268	4	2828·808	4	2549·616	6
3314·746	6	3045·082	4	2817·506	3	2543·927	5
3298·137	5	3040·430	4	2813·288	9	2535·610	6
3292·029	5	3030·150	4	2797·777	4	2524·291	6
3280·268	5	3024·035	5r	2778·847	4	2512·366	4
3268·246	4	3011·484	4	2759·816	4	2507·904	4
3265·057	3	2990·394	4	2746·486	7	2496·539	5
3246·015	3	2987·293	5	2728·026	4	2474·818	5
3233·061	5	2976·130	4	2714·419	6	2468·885	5
3217·389	4	2959·996	4	2699·114	4	2453·478	4
3202·562	3	2941·343	8	2679·066	6	2443·871	4
3191·666	5	2926·584	5	2669·498	4	2413·313	6
3184·903	4	2912·161	8	2656·154	3	2406·663	6
3171·353	4	2899·418	4	2641·654	3	2399·244	6
3161·370	2	2887·808	4	2632·248	4	2389·979	4
3155·293	2	2874·176	7	2621·677	6	2380·763	4
3142·888	4	2866·629	4	2612·787	3	2375·193	4
3129·334	4						
3125·663	6						
3116·632	5						
3098·191	3						
3091·581	4r						

It is possible that with apparatus of small dispersion the iron arc spectrum may be found too complex for ordinary work, or it may be that the necessary electric current is not available. In such cases the electric spark may be employed between electrodes of cadmium, or of an alloy of cadmium, tin, and lead, made by melting the three metals together in atomic proportions. These sources were used by Hartley in his early investigations. It must be remembered that unless the precaution is adopted of using self-induction in the secondary circuit a spark spectrum is always contaminated by air lines, many of which are very prominent. On the other hand, a vacuum tube containing neon and

helium may be used and for work in the orange and red regions a vacuum tube containing neon only. A very convenient source for the neon spectrum is to be found in the neon lamp made by the General Electric Co., England.[1] These lamps require a direct current supply of either 250 to 220 volts, or 220 to 200 volts, and are made to fit the ordinary lamp socket. They possess an average life of 300 hours.

The secondary standards in the neon spectrum were given on p. 37, and in addition to these the following wave-lengths may be quoted [2] :—

8495·380	7059·111	3600·170	3460·526
8377·606	7024·049	3593·634	3454·197
8300·369	6929·468	3593·526	3447·705
8136·408	6402·245	3520·474	3417·906
7544·050	5820·155	3515·192	3369·904
7535·784	5764·419	3501·218	
7488·885	5400·562	3498·067	
7438·902	5341·096	3472·578	
7245·167	5330·779	3466·581	
7173·939	3633·664	3464·340	

The following wave-lengths of the helium lines may also be given [3] :—

7281·349	5015·675	4387·928	3888·646
7065·188	4921·929	4143·759	3819·606
6678·149	4713·143	4120·812	3705·003
5875·618	4471·477	4026·189	3613·641
5047·736	4437·549	3964·727	3187·743
			2945·104

It is very convenient to take a photograph of the standard spectrum chosen and calibrate it by marking as many as possible of the lines of known wave-length preferably by writing the wave-lengths against them on the plate. This saves endless trouble in future work and the plate serves as a reference plate. For the recognition in the first instance of the lines in a complex spectrum, the wave-length scale supplied with certain spectrographs, for example that illustrated in Fig. 62, is very useful but the scale must itself be previously calibrated. Even under the best conditions such a scale cannot be used for the determination of wave-lengths, but when calibrated it can be used for the recognition of lines in a complex spectrum. The calibration is very easy to carry out with the help of some simple spectrum, such as that of the cadmium spark or that of the helium vacuum tube. The spectrum is photographed with the scale alongside it and the apparent wave-lengths of the lines are read off on the scale. The errors in wave-length are then plotted on squared paper against the scale readings and in this way a curve of errors for the scale is obtained. The complex spectrum is then photographed with the scale alongside it and the wave-lengths of the lines read off and corrected from the curve of errors, the values being then sufficiently accurate to recognise them in the list of their wave-lengths.

[1] Sole agents, Adam Hilger, Ltd., London.
[2] Bureau of Standards, Bulletin, 14, 765 (1918-19).
[3] *Ibid.*, 159 (1918-19).

If the wave-length scale is not available, recourse may be had to a map of the spectrum, the groups of lines being readily recognised. An exceedingly valuable reference book is the *Atlas of Spectra*, published by Hagenbach and Konen.[1] In the case of the spectrum of the iron arc the photographic enlargement of this spectrum with wave-length scale, published by Hilger, may be used.

In any comparison with a standard map of a spectrum taken by means of a prism spectrograph, it must be remembered that as one proceeds along the prismatic spectrum towards the blue, the dispersion continually increases, so that a given linear distance on the plate represents a smaller and smaller change in the wave-length and *vice versâ.*

A description may be here given of the micrometer apparatus used in all linear measurements of photographs of spectra.

The most common type in use is the travelling microscope, which consists of a microscope mounted on a slide which accurately works in grooves, and is actuated by a micrometer screw. The length of travel of the slide is usually about six inches, which is quite sufficient for all ordinary work. The micrometer screw, which is cut and corrected as described on p. 27, is mounted on the frame of the instrument, and works in bearings so that it cannot move backwards or forwards; it is provided with a large divided drum-head and also a milled wheel or handle for turning it. The drum-head is, as a rule, divided into a hundred divisions, which can easily be read to a tenth of a division, so that, if the screw is cut with a pitch of one millimetre, the movement of the microscope can be read to a thousandth of a millimetre. The whole is fixed to a massive stand in order to have the instrument as rigid as possible. Under the microscope is a support upon which the plate rests, and there is also provided a travelling mirror for illumination. The microscope proper is of quite low power, usually about twenty diameters; if a higher power be used the spectrum lines will become too magnified and difficult of measurement. The instrument is shown in Fig. 70.

In the eyepiece of the microscope, which is of the Ramsden design, one or two spider webs are fixed, one of which in taking a reading is adjusted upon the centre of the spectrum line. Under the best conditions of definition and sharpness of spectrum lines it is possible to determine the position of a line to 0·001 mm. Kayser[2] has designed a similar micrometer which is provided with certain mechanical arrangements, by means of which the reading of the micrometer and the intensity of the lines can be printed upon paper tapes; this is done by pressing certain keys similar to those of a typewriter so that the eye need not be removed from the microscope during the measurement of a plate.

When only small linear distances have to be measured very good results can be obtained by the use of an ordinary travelling wire micrometer eyepiece (see Fig. 42, p. 95) fitted to a low-power microscope.

[1] *Atlas of Emission Spectra of Most of the Elements.* A. Hagenbach and H. Konen. Authorised English Translation by A. S. King. W. Wesley & Son, London, 1905.

[2] *Handbuch der Spectroscopie*, i. 644.

The range of this instrument is, of course, very limited, being only a few millimetres on the plate, but it serves very well in interpolation measurements when the reference lines in the standard spectrum are situated close together.

In Fig. 71 is shown the Zeiss stereo-comparator, an instrument eminently suitable for measuring spectrum plates when the greatest possible accuracy is required. The fundamental principle of the instrument lies in the stereoscopic comparison of the unknown spectrum with a standard. It is too complex to describe in detail.

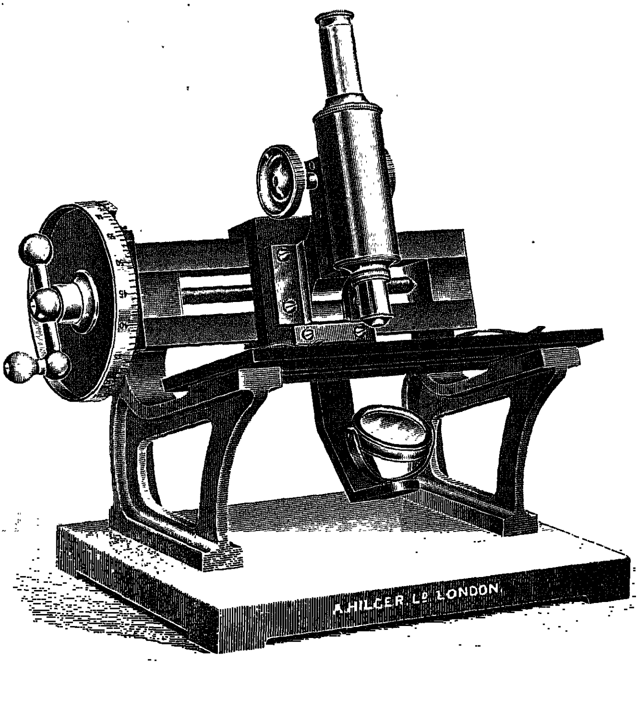


FIG. 70.

In the older forms of instrument two microscopes are employed, involving the use of both eyes. In the modern form of this instrument the two microscopes have been superseded by a Blink microscope, as is shown in Fig. 71. In Fig. 72 is reproduced a photograph taken with this instrument of two spectra in the same field of view.

Before proceeding to measure any photograph for the determination of wave-length, it is necessary to test each one with the view of finding whether the standard and the unknown spectra are correctly situated with regard to each other. In order to permit of this being done, it is

advisable to arrange that the unknown spectrum should show some known lines; for example, in the case of a gas in a vacuum tube a small quantity of hydrogen may be allowed to be present, or, again, in the case of spark spectra the air lines will serve the same purpose.

In spark spectra also one electrode may consist of a metal the spectrum of which is perfectly known, whilst the other electrode consists of an unknown substance. These known lines are picked out and their wave-lengths determined by reference to the standard spectrum. If the values so found agree with the known values, well and good; if not, the plate is of little use. It is true that we may construct a table of errors to be applied to the new spectrum, but this is a risky proceeding. When some good plates have been obtained in which the two spectra are correctly placed, these may be measured. It is first of all advisable to write on each plate the wave-lengths of as many as possible of the lines of the standard spectrum which may be found by comparison with the reference plate described above.

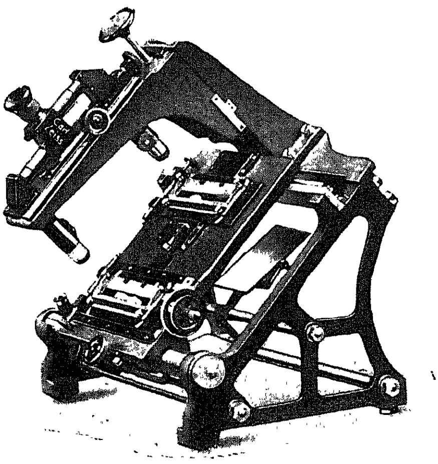


FIG. 71.

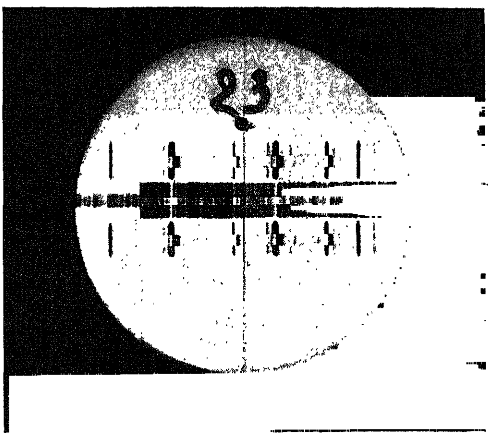


FIG. 72.

As has been stated several times before, the wave-length of any line is determined by measuring its position relatively to two lines, one on each side of it, in the standard spectrum. Although the dispersion continually increases in the spectrum as the blue is approached, yet in practice, if the two reference lines be situated close enough together, a simple linear interpolation will give the wave-length of the unknown line with sufficient accuracy. It is important, therefore, that the standard spectrum should contain as many lines as possible, so that, whatever be the wave-length of the unknown line, there will always be found lines in the standard situated sufficiently close to it to render its accurate measurement possible. It is advisable in actual work to select more than two of the lines in the standard, which should all be measured together with the unknown line; the wave-lengths of all should be computed by interpolation between those of the two extreme lines taken in the standard, so that the values found for the intermediate standard lines can be compared with the known values. This puts a check upon the accuracy of the measurements.

In view of the adoption of the new international standard of wave-lengths it is now obviously necessary to express all observations in terms of that standard. For this reason the standard spectrum employed should preferably be that of the iron arc, supplemented by that of neon. The wave-lengths of the lines of these spectra have already been given on pages 38 and 134. If other sources are used as standards, then it must be recognised that the accuracy will not be so great but will probably be sufficiently good for all ordinary purposes. Beyond the standard wave-lengths which have been quoted, relatively few direct measurements on the new standard scale have been made of the wave-lengths of the spectrum lines of elements. A complete list of the wave-lengths on Rowland's scale of the spectrum lines of all the elements is given by Kayser, and he also gives a table of corrections which must be subtracted from wave-lengths on the Rowland scale in order to reduce them to the international standard. The following table of corrections may be given:—

Region.	Subtract.	Region.	Subtract.	Region.	Subtract.
8800 to 8300	0·35	6500 to 6050	0·21	4150 to 3450	0·15
8300 to 8200	0·31	6050 to 5500	0·22	3450 to 3250	0·14
8200 to 8000	0·30	5500 to 5400	0·21	3250 to 3125	0·13
8000 to 7700	0·29	5400 to 5375	0·20	3125 to 2950	0·12
7700 to 7400	0·28	5375 to 5325	0·19	2950 to 2800	0·11
7400 to 7200	0·27	5325 to 5300	0·18	2800 to 2625	0·10
7200 to 7000	0·26	5300 to 5125	0·17	2625 to 2475	0·09
7000 to 6850	0·25	5125 to 4550	0·18	2475 to 2300	0·08
6850 to 6750	0·24	4550 to 4350	0·17	2300 to 2150	0·07
6750 to 6570	0·23	4350 to 4150	0·16	2150 to 1950	0·06
6570 to 6500	0·22				

The corrections between 7000 A. and 1950 A. are those given by Kayser,[1] whilst those between 8800 A. and 7000 A. are given by Meggers.

[1] *Handbuch der Spectroscopie*, vi. 891.

In drawing up this table Kayser compared the interferometer standards with Rowland's measurements of the same lines in the solar spectrum, but this is not very satisfactory, since, as has already been stated, the solar wave-lengths are open to objection. On the other hand, Fabry and Perot[1] made interferometer measurements of certain solar lines and from a comparison of these with Rowland's values the following list of corrections is obtained, but this only extends from 6400 A. to 4600 A. :—

Region.	Subtract.	Region.	Subtract.
6400 to 6260	0·21	5405 to 5395	0·19
6260 to 6040	0·20	5395 to 5340	0·18
6040 to 5940	0·21	5340 to 5250	0·17
5940 to 5660	0·22	5250 to 5000	0·16
5660 to 5520	0·21	5000 to 4800	0·17
5520 to 5405	0·20	4800 to 4600	0·16

The difference between the two tables in the region common to both is not serious, and as Hartmann[2] shows the error liable to be introduced in using the first table for wave-lengths smaller than 8300 A. will not exceed 0·02 A. and usually not more than 0·01 A. In the range 8800 A. to 8300 A. the error may reach as much as 0·04 A.

Reference may also be made to the admirable tables published by the late Dr. Marshall Watts under the title of *Index of Spectra.* Whereas in the original volume the wave-lengths were expressed on Ångström's scale, the various appendices contain the wave-lengths expressed on Rowland's scale.

Care must be taken in making the measurements of a spectrum photograph to adjust the plate properly under the microscope, and to see that the direction of travel of the microscope is parallel to the spectrum, or rather the junction of the two spectra. Another very important point to be remembered is the necessity of guarding against backlash in the measuring instrument, for all these instruments show it to a certain extent; the nut working upon the micrometer screw and carrying the microscope is never tightly clamped upon the screw, with the result that if, after turning the screw in one direction, the motion be reversed, an appreciable fraction of a whole turn will have to be given to the screw before the nut starts moving back. For this reason it will be found that with a travelling micrometer different readings will be obtained, if one approach the line from first one side and then the other. It is necessary, therefore, in measuring the lines, always to approach them all from the same side, that is, of course, the side nearest the starting-point.

In making an actual measurement, the cross-wire in the eyepiece is moved forwards until it be judged to bisect the chosen line; if by any chance it be moved too far, it must be brought back some distance and

[1] *Ann. Chim. Phys.*, **25**, 98 (1902).
[2] *König. Gesell. der Wiss. Göttingen*, Abh., **10**, No. 2 (1916).

the line approached again. When a sufficient number of lines in the standard spectrum have been selected for the purpose of comparison with the lines to be measured in the unknown spectrum, the first of these is carefully adjusted under the cross-wire of the eyepiece of the micrometer, when set at zero. It is a good plan to label the chosen standard lines in some way, so that they can be recognised through the microscope, as otherwise mistakes may occur when the standard is very complex. When the first standard line is properly adjusted, the microscope is moved along the whole length of spectrum required, or as much as is possible, each chosen standard line and each unknown line being measured on the way.

A considerable amount of trouble is saved by using a travelling microscope with a long travel, even with prism photographs, because of the fewer times that the plate has to be moved and readjusted under the zero of the instrument. If, however, a micrometer with a very short travel is employed, as, for example, a travelling wire micrometer eyepiece, then the photograph must be frequently moved, and a new standard line adjusted under the zero of the instrument. In calculating the wave-lengths from the measurements of the lines, proportional parts are taken between two standard lines which are not very far apart. For example, the following may serve as a typical record of measurements of a spectrum, the standard of comparison being the arc spectrum of iron, Rowland's scale:—

Scale reading of micrometer.	Wave-lengths of standard iron lines.	Proportional parts of wave-lengths.	Wave-lengths.	Errors.
0	3821·32	0	(3821·32)	
337		1·82	3823·14	
420		2·27	3823·59	
604	3824·58	3·27	3824·59	+ 0·01
934		5·04	3826·36	
1024		5·53	3826·85	
1229	3827·96	6·62	3827·94	− 0·02
1561		8·42	3829·74	
2047		11·04	3832·36	
3727		20·11	3841·43	
3814		20·58	3841·90	
4092	3843·40	{(22·08) 0}	(3843·40)	
4829		3·98	3847·38	
5045		5·15	3848·55	
5339	3850·11	6·73	3850·13	+ 0·02
5413		7·14	3850·54	
6104		10·83	3854·23	
6518	3856·49	13·09	3856·49	0·00
6891		15·10	3858·50	
7356		17·61	3861·01	
8216	3865·65	(22·25)	3865·65	

The first column contains the scale readings of the micrometer, and the second column the wave-lengths of the iron lines which were

PLATE I.

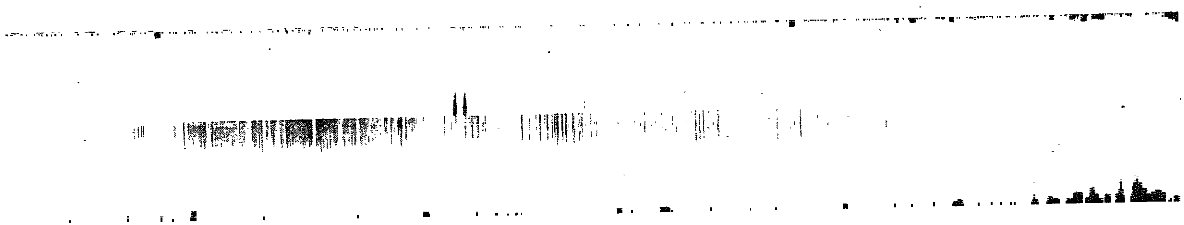


FIG. 73.

[To face page 141.

measured *en route.* In the third column are the proportional parts expressed in wave-lengths; these have been calculated in two sections, between the two iron lines $\lambda = 3821{\cdot}32$ and $\lambda = 3843{\cdot}40$, and between $\lambda = 3843{\cdot}40$ and $\lambda = 3865{\cdot}65$. The first proportional part is therefore equal to—

$$\tfrac{337}{1002} \times (3843{\cdot}40 - 3821{\cdot}32) \text{ Ångström units,}$$

and the second to—

$$\tfrac{420}{1002} \times (3843{\cdot}40 - 3821{\cdot}32), \text{ and so on.}$$

The fourth column contains the computed wave-lengths; these are obtained by addition of the proportional parts to 3821·32 in the first section, and to 3843·40 in the second section. The wave-lengths of the intermediate iron lines are calculated along with the rest, and the fifth column contains the errors in these wave-lengths. It will be readily seen that these errors will give a general idea of the accuracy of one's work, for the presumption is, *ceteris paribus,* that the same order of error is affecting the measurements in the unknown spectrum.

In Fig. 73 is reproduced a photograph of two spectra in juxtaposition, which may give an illustration of the method of interpolation described above. The spectrum on the right hand is part of the arc spectrum of iron, while the other, the arc spectrum of copper, may serve as the unknown, the wave-lengths of which have to be determined. The plate is mounted under the microscope so that the junction of the two spectra is in the middle of the field of view, and also that the travel of the microscope is parallel to this line of junction.

For a determination of the wave-lengths of the lines in a spectrum Hartmann's interpolation formula is exceedingly useful. The accuracy of the results given by any interpolation formula depend, of course, on the range of wave-lengths over which it is used. If this range be not too great then the results are surprisingly accurate. Although for the determination of unknown wave-lengths with the highest accuracy it is preferable to work by the method of linear interpolation between a number of standard lines, yet the Hartmann formula is capable of giving results sufficiently accurate for many purposes. It is particularly suited, for example, for the recognition of all the lines in a standard spectrum such as that of the iron arc.

The formula in its most general form is as follows:—

$$\lambda = \lambda_0 + \frac{c}{(n - n_0)^{\frac{1}{a}}}$$

where λ_0, c_1, n_0, and a are constants. Hartmann, however, has pointed out that if too great ranges of wave-lengths are not required, the constant a, which is about 1·2, may be omitted, which simplifies the calculations very considerably. In the place of the indices of refraction n we may use the angular deviation as given by the prism, or, what comes to the same thing, the linear distances between the lines in a

photographed spectrum. If we read the linear distances in a photographed spectrum by means of a travelling micrometer, these readings may be substituted in the formula—which then may be written—

$$\lambda = \lambda_0 + \frac{c}{d_0 - d}$$

or

$$\lambda = \lambda_0 + \frac{c}{d - d_0}$$

according to the direction in which the plate is measured; d is the reading of the lines on the linear scale defined by the micrometer. Hartmann[1] further points out that λ_0 is a constant for any spectroscope, and may be determined once and for all, whilst the constant d_0 simply represents some definite point on the linear scale.

The calculation of the three constants λ_0, c, and d_0 is very simple; it is only necessary that the wave-lengths and scale readings of three lines be known. In the table below are given the scale readings and the wave-lengths of the lines in a stellar spectrum photograph which are taken from Hartmann's paper. If we select three of these, the constants may at once be found. Let us take, for example, the three lines, the wave-lengths of which are $\lambda = 370{\cdot}96$, $\lambda = 414{\cdot}39$, $\lambda = 486{\cdot}17$, and the corresponding scale readings $d = 0$, $d = 101{\cdot}513$, and $d = 195{\cdot}729$, respectively. We then have the three equations

$$370{\cdot}96 = \lambda_0 + \frac{c}{d_0 - 0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$414{\cdot}39 = \lambda_0 + \frac{c}{d_0 - 101{\cdot}513} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$486{\cdot}17 = \lambda_0 + \frac{c}{d_0 - 195{\cdot}729} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then by subtraction of (1) from (2)

we have $$43{\cdot}43 = \frac{c}{d - 101{\cdot}513} - \frac{c}{d_0}.$$

By multiplying up and rearrangement of terms

we get $$d_0^2 - 101{\cdot}513d_0 = \frac{101{\cdot}513}{43{\cdot}43}c = 2{\cdot}33739c \quad . \quad . \quad . \quad (4)$$

Similarly, by subtraction of (1) from (3)

we have $$d_0^2 - 195{\cdot}729d_0 = 1{\cdot}69889c \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Subtract (5) from (4)

we have $$94{\cdot}216d_0 = 0{\cdot}63850c$$

whence $$c = 147{\cdot}56d_0.$$

Substitute this value of c in equation (1)

then $$370{\cdot}96 = \lambda_0 + 147{\cdot}56$$

whence $$\lambda_0 = 223{\cdot}40.$$

[1] *Astrophys. Journ.*, 8, 218 (1898).

Again, substitute this value of λ_0 in equation (2)

then
$$414{\cdot}39 = 223{\cdot}40 + \frac{147{\cdot}56}{d_0 - 101{\cdot}513}$$
whence
$$d_0 = 446{\cdot}414 \text{ and } c = 65{,}872.$$

In this way we have obtained the values of the three constants; from these the wave-lengths of all the remaining lines may be calculated from their scale readings by means of the formula—

$$\lambda = 223{\cdot}40 + \frac{65{,}872}{446{\cdot}414 - d.}$$

These calculated wave-lengths are given in the second column of the table, and the differences between these and the true values are given in the fourth column.

Scale reading.	λ in μμ (calc.).	λ in μμ (obs.).	Errors.
0	370·96	370·96	—
5·336	372·75	372·71	+ 0·04
5·529	372·81	372·77	+ 0·04
10·134	374·39	374·36	+ 0·03
11·504	374·86	374·85	+ 0·01
14·698	375·98	375·95	+ 0·03
15·291	376·19	376·15	+ 0·04
16·425	376·62	376·58	+ 0·04
22·612	378·83	378·80	+ 0·03
24·557	379·54	379·50	+ 0·04
25·780	380·00	379·97	+ 0·03
29·343	381·34	381·31	+ 0·03
35·905	383·86	383·85	+ 0·01
36·547	384·12	384·10	+ 0·02
42·761	386·59	386·58	+ 0·01
45·902	387·86	387·86	± 0·00
50·040	389·58	389·57	+ 0·01
51·796	390·32	390·32	± 0·00
52·401	390·58	390·58	± 0·00
56·460	392·32	392·30	+ 0 02
57·620	392·83	392·82	+ 0·01
63·266	395·32	395·30	+ 0·02
65·167	396·18	396·17	+ 0·01
74·555	400·54	400·52	+ 0·02
82·883	404·62	404·60	+ 0·02
86·430	406·38	406·39	− 0·01
93·748	410·19	410·19	± 0·00
101·513	414·39	414·39	—
111·722	420·21	420·21	± 0·00
115·891	422·70	422·70	± 0·00
123·144	427·16	427·17	− 0·01
128·804	430·80	430·80	± 0·00
133·741	434·07	434·07	± 0·00
139·993	438·37	438·37	± 0·00
142·999	440·50	440·50	± 0·00
175·785	466·80	466·80	± 0·00
195·729	486·17	486·17	—

It will be seen on reference to the column of errors that there is a general trend beginning with an error of $0{\cdot}04\mu\mu$ and ending with no error at all. Hartmann has also calculated the wave-lengths of these lines in his paper, using three wave-lengths just as was done above. He, however, does not state which lines he used, and it happens that the scale reading of the first line on the list was slightly wrong in Hartmann's measurements, which accounts for the general trend of errors in the above table. I give the results of my calculations, however, because they show very conclusively what is to be expected if one of the three lines chosen happens to have been inaccurately read with the micrometer. It is hardly necessary to point out that it would be a very simple matter to construct a curve of errors from the above values by means of which they could be smoothed out to give an equally distributed error. This is a very much simpler matter than a series of calculations to find out which three lines give the most even distribution of error.

In exactly the same way may the formula be applied to the measurements of the deviations given by a prism. For example we may take the wave-length curve reproduced on page 130, and calculate its constants.

Three readings on this curve are—

$$\begin{aligned}
\lambda &= 7800\ \mathrm{D} = 47^\circ\ \ 0' = 2820 \text{ minutes.}\\
\lambda &= 5400\ \mathrm{D} = 48^\circ\ 20' = 2900 \quad ,,\\
\lambda &= 4200\ \mathrm{D} = 50^\circ\ 20' = 3020 \quad ,,
\end{aligned}$$

For the sake of simplicity we may subtract 2820 from these readings of minutes, and then we have 0, 80, 200, or more simply 0, 8, 20, if we adopt ten minutes as the unit. From these equations we readily find the constant to be $\lambda_0 = 2400$, $c = 54{,}000$, and $D_0 = -10$. These will then be found to fit the curve with a very fair accuracy.

These examples will doubtless suffice to show how the formula is applied and how serviceable it can prove. The accuracy obtainable with this formula is very materially increased if the region of the spectrum covered is not too large. On page 60 the formula in its simpler form was applied to the indices of refraction of a glass over the whole range of the visible spectrum, 7600 A. to 4000 A., and the results obtained were remarkably accurate, the maximum error being about 1 in 40,000. Occasion has been found recently to test the accuracy on some fine line absorption spectra taken in Liverpool and it was found that, when the region of the spectrum dealt with is not greater than about 200 Ångströms, the accuracy is equal to that obtained in the actual reading of the spectrum lines themselves.

An interesting application has been made of this formula by Fowler and Eagle.[1] If a prismatic photograph of a spectrum be copied by means of a camera lens, then it is possible to obtain the lines in the copy distributed according to their wave-lengths, *i.e.* it is possible to obtain a normal spectrum. This is done by setting the spectrum plate

[1] *Astrophys. Journ.*, **28**, 284 (1908).

and the plate on which the image is received at certain angles to the axis of the lens of the copying apparatus. Fowler and Eagle show how these angles may be calculated if the focal length of the lens be known, and also the constants of Hartmann's formula for the spectrum in question.

In measuring the lines in a spectrum notes should be made of the intensity or brightness in each case. The estimation of the intensity of lines in an emission spectrum is troublesome, owing to there being no satisfactory method of comparison; as a general rule, we mark the lines of greatest brightness as having an intensity of 10, and the weakest as having an intensity of 1; the other lines are then given an intensity varying from 9 to 2, depending upon their estimated brightness. On the other hand Kayser in his *Handbuch* adopts as the scale of brightness 20 to 1 and this has some advantages since it allows a greater margin in the expression of intensity. There is no method of measuring the intensity of lines except by the use of a photoelectric cell or thermopile and galvanometer. The recorded intensities therefore are as a rule arbitrary and it will be found that observers sometimes differ considerably in the values they assign to the intensity of a line. It must not be forgotten that sometimes a line of an emission spectrum is reversed in a photograph, the central portion of the line being wanting on the plate; in measuring the position of such a reversed line, it is needless to point out that the middle of the transparent centre must be taken, as this, of course, represents the centre of the true line. There are present in the spectra of certain metals lines which are diffused and others which are diffused upon one side only, the other side being perfectly sharp and well-defined. When lines of the latter type undergo self-reversal, the position of the true centre of the line is often very difficult to estimate, and great care must be taken to avoid making serious errors. No rule can be given for finding the centre of such a line; one can only be guided by the general appearance of the line. The accuracy of measurement of such lines, and all diffused lines generally, is clearly lower than in the case of fine and well-defined lines.

An ingenious method has been described by Miss Riwlin[1] for measuring the intensities of lines as recorded by a photographic plate, the method having been worked out in Professor Ornstein's laboratory at Utrecht. By means of a lens an image of a convenient light source is focussed on to the spectrogram, and a second lens forms an image of the spectrum on a slit, behind which is placed a thermopile connected with a Moll galvanometer (see p. 255), care being taken that the image of each spectrum line is exactly parallel to the slit. The excursion of the light reflected from the galvanometer mirror is directly proportional to the intensity of the light energy falling on the thermopile and hence inversely proportional to the intensity of the image of the spectrum lines in the negative. The whole apparatus is automatic in its working, since

[1] Rassa Riwlin, *Das Wesen der Lichtzerstreuung in flüssigen Kristallen*, van Druten, Utrecht, 1923.

the photograph of the spectrum is moved by clockwork with constant speed at right angles to the spectrum lines, and the light spot from the galvanometer is focussed on to a broad strip of sensitive photographic paper which is moved synchronously with the photographic plate. This strip of photographic paper, on development, gives a complete and permanent record of the intensities of the spectrum lines.

A simple and ingenious method of approximately determining the wave-lengths of lines in photographs of prismatic spectra has been devised by Edser and Butler.[1] This method consists in photographing a series of interference fringes, adjacent to the spectrum to be measured; these interference fringes are produced by Fabry and Perot's method, which consists in causing a beam of white light to pass through a film of air bounded by two parallel sides of half-silvered glass. When this light is examined in a spectroscope, a continuous spectrum is seen, crossed by a series of interference fringes, the theory of which will be dealt with at length in Volume II., Chapter I. A sufficiently accurate interference apparatus can be made by taking two pieces of good plate-glass about 3 inches square, which are each half silvered on one face;[2] the plates are then carefully dried and mounted together, the two silvered faces turned towards one another. The plates are fastened together by a little soft wax placed all round the edges, when perfect adjustment can be obtained by simply pressing the plates together with the fingers. A preliminary adjustment for parallelism is made as follows: a spot of light or an incandescent electric lamp is viewed through the silvered surfaces; a long train of images due to multiple reflections is generally visible. These images are brought into coincidence and then, on examining a sodium flame through the apparatus, interference bands will generally be visible. The final adjustment for parallelism is made with the help of these bands which should be made as broad as possible. In carrying out this adjustment, the film is held as close as possible to the eye, because for a parallel air film viewed normally the interference bands are formed at an infinite distance. The perfection of the results finally obtained will depend greatly on the accuracy of this adjustment.

Directions for making a simple interference apparatus suitable for this purpose are given by Barnes.[3]

The slit of the spectroscope is illuminated by a slightly convergent beam of light from an arc lamp, and the plates are placed in front of the slit, and as near to it as possible; under these circumstances the spectrum will be found to consist of a series of bright lines separated by black intervals. The best results will be obtained when the plates are in such a position that the slit is parallel to the direction of the interference bands seen with sodium light. The closeness of the bands depends upon the thickness of the film between the silvered surfaces. It

[1] *Phil. Mag.*, **46**, 207 (1898).

[2] See Vol. II., Appendix. By half silvering is meant the deposition of a silver layer which is transparent to light and yet is dense enough to reflect a considerable portion.

[3] *Nature*, **80**, 187 (1909).

s well to introduce some common salt into the arc in order to obtain he D lines, as well as the H and K lines superimposed upon the fringes. By means of draw slides, or screens upon the slit, these interference bands are photographed adjacent to the spectrum which is to be measured.

As the interference bands are due to the interference of the directly ransmitted ray, and that twice reflected from the surfaces of the film, t follows that, if d be the thickness of the air film, and n the refractive ndex (supposed independent of wave-length)—

$$2nd = x\lambda_0 = (x + 1)\lambda_1 = (x + 2)\lambda_2 \ldots = (x + y)\lambda_y$$

where λ_0, λ_1, λ_2, λ_y, etc., are the wave-lengths corresponding to the bright bands, and x is some whole number. We have, therefore—

$$x\lambda_0 = (x + y)\lambda_y,$$

whence

$$x = \frac{y\lambda_y}{\lambda_0 - \lambda_y} \quad \ldots \ldots \ldots \quad (1)$$

where the band corresponding to λ_y is the yth towards the violet from that corresponding to λ_0. We have, also, therefore—

$$\lambda_r = \frac{x\lambda_0}{x + r}, \quad \ldots \ldots \ldots \quad (2)$$

where λ_r is the wave-length corresponding to the rth band counting from the band λ_0.

As an example, Edser and Butler found, that on a particular photograph the following figures were obtained :—

Scale-reading 90·2, wave-length 5328·5(λ_0),
" " 402·3, " 3968·6(λ_y).

Then, in equation (1)—

$$y = 402{\cdot}3 - 90{\cdot}2 = 312{\cdot}1$$

and

$$\lambda_0 - \lambda_y = 1359{\cdot}9,$$

and therefore

$$x = 910{\cdot}8.$$

Again, to find the wave-length of the line, the scale reading of which is 371·2. Then, in equation (2)—

$$r = 371{\cdot}2 - 90{\cdot}2 = 281$$

and

$$\lambda = \frac{910{\cdot}8 \times 5328{\cdot}5}{910{\cdot}8 + 281} = 4072{\cdot}2.$$

The true wave-length of the line was 4071·8, giving an error of +0·4 tenth metres. With a finer scale more accurate results can be obtained.

When many lines have to be measured a graphical method may be adopted. If we write $\frac{1}{\lambda} = L =$ the wave number, we obtain the simple

relation, $\frac{x + r}{L}$ = constant, or $L = K(x + r)$. In other words, the wave number is a linear function of r, *i.e.* the relation between L and r may be expressed by a straight line. The wave numbers of a few lines at each end of the photograph are plotted against their scale readings, and a straight line is drawn through the points thus obtained. From this straight line the wave number of a line can be found at once from its scale reading.

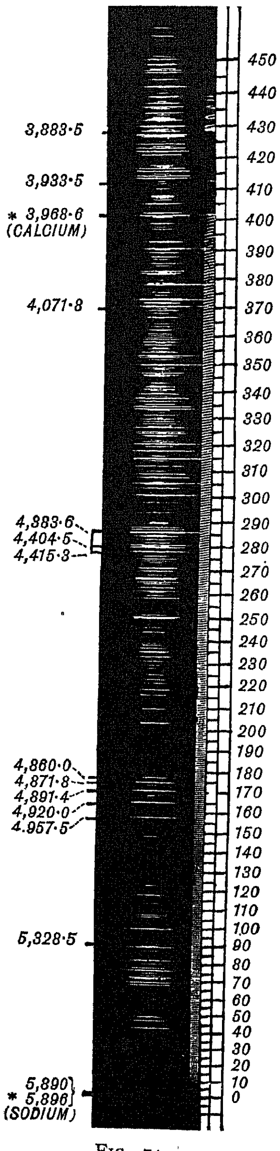


FIG. 74.

There is no need to take a separate photograph of the interference scale for every spectrum to be measured, for it is clear that this will be always the same, provided that the adjustments be not altered. in any way. If the D lines are superposed on the original interference scale, and occur in every succeeding spectrum photograph, it is only necessary to fit the interference scale on to the spectrum photograph so that the D lines coincide; the position of the spectrum lines can then be read on the scale with perfect accuracy.

A prism photograph, with the bands adjacent to it, is shown in Fig. 74.

Since the International Astronomical Union have approved as a method for the determination of the wave-lengths of tertiary standards interpolation measurements made between secondary standards on spectrum photographs taken with prism spectrographs, a short account may be given of the procedure to be adopted in computing the values of such wave-lengths. It is needless to point out that for work of the highest accuracy a spectrograph of great dispersion and resolving power must be used, and for this purpose an instrument such as that described on page 177 and illustrated in Fig. 63 may be recommended. The essential point to be noted is the advisability of the drawing of a curve of errors from the measurements made from the spectrograms. By means of a stereo-comparator or a travelling microscope a considerable length of the photographed spectrum can be measured, starting, of

ourse, from a secondary standard line and ending from a secondary tandard line. All the secondary standards, together with those lines the vave-lengths of which have to be determined, are measured, and the vave-lengths of all are calculated by linear interpolation between the irst and last secondary standard lines. The calculated wave-lengths of the secondary standards are then compared with their known wave-engths, and the differences found are plotted on squared paper against heir scale readings given by the comparator or the travelling microscope. In the first place, the smoothness of this curve and the general lie of the various points in relation to it give at once a measure of the accuracy of he determinations, and complete confidence can only be felt therein when a smooth curve is obtained. In the second place, from this curve of errors the corrections can be read which must be applied to the calcu-ated wave-lengths of the unknown line in order to obtain their true wave-lengths. This method of work eliminates almost all errors in the neasurements of a given plate; because such will be revealed by the general shape of the curve. There are two possible errors, however, which cannot be eliminated from the measurements of a single photo-graph. The position of an unknown line may be wrongly measured by accident—such a mistake in the position of a standard line will at once be recognised from the curve. Again, owing to a flaw in the photo-graphic plate, such as a depression in the emulsion, a line may be dis-placed from its correct position in the photograph, if the photographic plate is set at an angle to the optic axis of the spectrograph. These last two possible errors can only be detected by the measurement of several photographs of the same region of the spectrum. In each case the same procedure is adopted and the various determinations of the wave-length of each unknown line are compared together. If there is no reason to doubt the inherent accuracy of any of these, the mean of them all will have the greatest probable accuracy. If any value differs markedly from the others it should be rejected.

This is the method to be adopted but it must be remembered that all work of the highest accuracy demands the skill which can only be gained from understanding and experience. Understanding of the pos-sible variations due to the many sources of error, and experience which alone can teach the best methods of reducing all these to a minimum. At the outset many will find keen disappointment their portion, and in-deed at times, as the late Lord Rayleigh said, one is tempted to doubt the constancy of Dame Nature herself. But there comes at length to all who possess true love for her a great and uplifting sense of victory over the many pitfalls with which she bestrews the way of the unwary. To such is born a very perfect happiness, the birthright of the true scientist who, without thought of personal gain, follows new paths, and, seeking inspiration at the fountain's head, extends the confines of knowledge for the benefit of mankind.

CHAPTER VI.

THE DIFFRACTION GRATING.

General Theory.—The elementary theory of the production of spectra by means of the diffraction grating was treated in the introductory chapters, and it was shown that the general wave-length equation has the form—

$$n\lambda = b(\sin i + \sin \theta), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n stands for the number of the order of the spectrum, λ the wave-length, b the grating space, i the angle of incidence, and θ the angle of diffraction. When the incident rays are normal to the grating the equation is simplified to the form—

$$n\lambda = b \sin \theta.$$

Equation (1) readily gives an expression for the dispersion of a grating, for, if we assume the angle of incidence to be constant, then by differentiation we have—

$$nd\lambda = b \cos \theta d\theta$$

and thus
$$\frac{d\theta}{d\lambda} = \frac{n}{b \cos \theta}.$$

The dispersion of a grating, therefore, is equal to the number of the order of the spectrum divided by the product of the grating space into the cosine of the angle of diffraction. It is evident from this that the dispersion reaches a minimum value when $\cos \theta$ is a maximum, that is to say, when $\cos \theta = 1$, *i.e.* when $\theta = 0$. We see, therefore, that, when the observing telescope is placed perpendicular to the plane of the grating, the dispersion is a minimum and is equal to $\frac{n}{b}$.

Under these circumstances $d\theta$ = const. $\times$ $d\lambda$, and therefore small changes in λ produce proportional changes in θ, or, in other words, the spectrum obtained is perfectly normal. Although this is only strictly true when $\cos \theta = 1$, yet, as $\cos \theta$ varies so little from this with small changes in θ, it holds good for some distance on each side of the normal. It is quite easy to calculate how far it is possible to work from the normal within a given limit of accuracy. For example, if the accuracy required is 1 part in 10,000, it is necessary that $\cos \theta$ do not have a smaller value than $1 - 0{\cdot}0001 = 0{\cdot}9999$, and, therefore, that θ have no larger value than $48'$. The spectrum is thus normal within 1 part in 10,000 when

the angle of diffraction is less than 48′; similarly, it may be found to be normal with an accuracy of 1 in 1000 when the angle of diffraction is less than 2° 34′.

The values of the dispersion when $\theta = 0$ may be calculated for gratings having the usual values of b. Gratings are usually ruled with 20,000, 14,438, or 10,000 lines to the inch, that is, 7874·022, 5684·255, or 3937·011 to the centimetre. The dispersions of the three types of gratings (when $\theta = 0$) are, therefore, $n \times 7874{\cdot}022$, $n \times 5684{\cdot}255$, and $n \times 3937{\cdot}011$. As an example, we may calculate the angular difference between the two D lines in the second order with a 20,000 line grating. Taking the difference in wave-length between the lines as $0{\cdot}006 \times 10^{-5}$ cm., the angle between them will be $2 \times 7874{\cdot}1 \times 0{\cdot}006 \times 10^{-5} = 0{\cdot}000945$, which is 3′ 15″ of arc. The English gratings ruled at the National Physical Laboratory have 14,400, 7200, 4800, or 3600 lines to the inch, that is 5669·296, 2834·648, 1889·765, or 1417·324 to the millimetre.

It can readily be seen from equation (1) that the spectra of different orders are superposed upon one another, for, with any position of the observing telescope, that is, with fixed values of i and θ, it follows that $\lambda^{i}, = 2\lambda^{ii}, = 3\lambda^{iii}, 4\lambda^{iv}$, etc., where λ^{i}, λ^{ii}, λ^{iii}, λ^{iv}, etc., are the wave-lengths in the first, second, third, fourth, etc., orders. The different orders are thus superposed upon one another, and the wave-lengths are inversely proportional to the numbers of the orders. On wave-length of 9000 A. in the first order are superposed 4500 in the second order, 3000 in the third, 2250 in the fourth, and similarly for other wave-lengths in different orders. It also follows in the same way that the linear lengths of the spectra are proportional to the numbers of the orders.

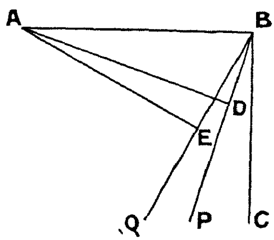


FIG. 75.

An expression for the resolving power of a grating was first given by Lord Rayleigh.[1] The resolving power of a spectroscope is defined as ratio $\frac{\lambda}{d\lambda}$, where $d\lambda$ is the difference in the wave-lengths of two lines just separated by the instrument, and λ the mean wave-length of the pair (*vide* p. 63 *et seq.*). Lord Rayleigh obtained the value of this expression as follows:—If in Fig. 75 AB represent the whole grating, and BP the principal direction of the diffracted rays for the wave-length λ in the nth spectrum, then, if the perpendicular AD be drawn, the length BD, or the relative retardation of the rays from the extreme grating apertures, will be equal to $mn\lambda$ if m be the number of apertures in the length AB. BQ is then drawn so that the projection of AB upon BQ, that is to say BE, is equal to $mn\lambda + \lambda$. Now, BQ will be the principal direction for a wave-length $\lambda + d\lambda$, and therefore BE must equal $mn(\lambda + d\lambda)$.

[1] *Phil. Mag.* (4), 47, 193 (1874).

It follows that—

$$mn\lambda + \lambda = mn(\lambda + d\lambda),$$

whence
$$\frac{\lambda}{d\lambda} = mn = r; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

or the resolving power of a grating is equal to the product of the number of apertures into the order of the spectrum. That the resolving power, or defining power, as it might be called, of a grating, depends upon the number of apertures follows from the elementary theory. If the retardation between the secondary waves from two adjacent apertures be equal to any odd number of half wave-lengths, they will mutually interfere; if, however, the retardation be not exactly equal to an odd or even number of wave-lengths, interference will take place between the waves from apertures which are not adjacent to one another. For example, if the retardation be equal to one-hundredth of a wave-length, the waves from the first and fifty-first apertures, the second and fifty-second, etc., will interfere, and, therefore, if the apertures be sufficiently numerous, total interference will take place, except when the retardation between the waves from adjacent apertures be equal to an exact number of whole wave-lengths; the greater the number of apertures, therefore, the better the interference on each side of a bright line, that is to say, the better the defining power of the grating. Again, if we start from equation (1) and multiply both sides of this equation by m, the number of rulings in the grating, we have—

$$mn\lambda = f(\sin i + \sin \theta)$$

where $f = bm =$ the width of the grating, being the product of the width of the grating spaces into the number of them.

By differentiation ($\sin i$ being constant)—

$$mnd\lambda = f\cos\theta d\theta,$$

and
$$mn = f\cos\theta\frac{d\theta}{d\lambda}.$$

Now, $f\cos\theta$ is the diameter of the beam of diffracted rays leaving the grating, and calling this a as before in the case of prisms (p. 63),

we have—
$$mn = a\frac{d\theta}{d\lambda}.$$

But from equation (2) $mn = \dfrac{\lambda}{d\lambda} = r$,

we see, therefore, that the resolving power of a grating is equal to the product of the aperture into the dispersion, and that the grating is quite comparable with other optical instruments.

If now in the equation $mn\lambda = f(\sin i + \sin\theta)$, r be substituted for mn,[1] then—

[1] Wadsworth, *Phil. Mag.* (5), 43, 317 (1897).

$$r\lambda = f(\sin i + \sin \theta)$$

and $$r = \frac{f}{\lambda}(\sin i + \sin \theta) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

This is an expression for the resolving power, which is independent of the number of rulings, and only dependent upon the aperture, and the position into which the grating is turned. The maximum value of r in (4) is obtained when $i = \theta = 90°$, in which case—

$$r_{\text{max}} = 2\frac{f}{\lambda}.$$

This theoretical maximum cannot, however, be obtained, as with very large values of the angles of incidence and diffraction the angular aperture of the grating becomes very small, and the light is reduced to a minimum. In practice the largest value of i when $\theta = 0$ is about 70°, and, in the Littrow type of instrument, when $i = \theta$ the value lies between 50° and 60°. The practical limit of resolving power lies, therefore, between $0{\cdot}94\frac{f}{\lambda}$ and $1{\cdot}64\frac{f}{\lambda}$. Taking the upper limit, we have for a $5\frac{1}{2}$-inch grating and $\lambda = 5500$ A. a resolving power of 410,000; that is to say, this grating should resolve lines the wave-lengths of which differ by 0·013 A. This, of course, is based on the assumption that the slit is infinitely narrow; this is never true in actual work, and the effect of this factor will be treated in Chapter IX.

It follows from equation (4), $r = \frac{f}{\lambda}(\sin i + \sin \theta)$, that, since θ and f are independent, the resolving power of a grating depends upon the extent of the ruled space, not upon the number of rulings in that space. From equation (2), $r = mn$, it would appear that r varies directly as m; but this equation assumes λ as constant, so that n is dependent upon m and θ. Hence the two equations are quite consistent.

It is of little use to increase the number of lines in a given space, because, for example, if two gratings be used of the same size, but one containing twice as many rulings as the other, the first order spectrum will be obtained with the first grating in the same position as the second order spectrum with the second grating; the resolving power will be identical in the two spectra. It thus follows that, provided the values of i and θ do not change, increasing the number of lines in unit length of grating surface does not increase the resolving power.

At the same time it may be noted that there are certain advantages to be derived from using a grating containing a great number of rulings rather than one which contains fewer. One is thereby enabled to work in the lower orders and still obtain high resolving power; as stated above, a grating with 20,000 lines to the inch will give the same resolving power in the first order as a grating of same size with 10,000 lines to the inch in the second order, because the values of the angles of incidence and diffraction are the same in each case. Now, two very decided

advantages would be obtained by using the 20,000 line grating and working with the first order. First, in all probability the amount of light will be greater in the first than in the second order, and second, there is less complication arising from superposition of spectra in the first order than in the second. Further consideration, perhaps, will render this second advantage more explicit. If we work in the first order spectrum we shall have the region from 2000 to 4000 A. practically free from contamination with higher orders, because superposed on it will be the second order spectrum from 1000 to 2000 A. which cannot under ordinary circumstances be photographed. The region from 4000 to 7000 A. will have superposed upon it the wave-lengths 2000 to 3500 A. in the second order, the third order being still photographically inactive. It is possible, therefore, to photograph the first order spectrum without any contamination with higher orders, from 2000 A. to at least 4000 A. and from 4000 A. to 7000 A., by using an absorbing layer of plate-glass, which will entirely cut off the superimposed second order.

When working in the second order, however, the contamination by the spectra of other orders is very troublesome, because it is impossible to photograph the second order in any region without the use of absorbing layers; in those regions where contamination by the third order is not prevalent, photographically active portions of the first order are superimposed, which, of course, cannot be removed by absorption, as there is no substance at present known which will absorb the higher wave-lengths and transmit the lower wave-lengths.[1] The great advantage accruing from the use of the first order spectrum, especially for work in the ultra-violet region, is thus very marked, and for this reason, as well as for the greater brightness of the first order spectrum, a grating with a greater number of rulings in unit length is to be preferred to one with a lesser number.

The brightness of the spectra of different orders next claims our attention; in this case we must deal with an ideal grating, that is to say, a grating which consists of alternate perfectly opaque and transparent portions, the theory of which was first worked out by Lord Rayleigh.[2] The grating, however, in practical use does not possess truly opaque portions, but translucent portions, so to speak, produced by cutting grooves on a glass or polished metal plate. Furthermore, these grooves may vary in shape, nature, and size from grating to grating and therefore the illumination obtained very often varies considerably from that produced by an ideal grating. The theory of the effect of varying the nature of the ruling has been worked out by Rowland very fully, and the abnormal results obtained in practice can be mathematically accounted for.

To consider the illumination produced in any spectrum given by a grating, let us first deal with that produced by a plain aperture, and after-

[1] Wood (*Phil. Mag.*, 5, 257 (1903)), has found that a gelatine film dyed with nitrosodimethylaniline absorbs portion of the visible spectrum and transmits the ultra-violet. This, however, does not modify the conclusions drawn in the text, as the use of such a screen very materially reduces the light, and is, therefore, not to be recommended.

[2] *Phil. Mag.* (4), 47, 193 (1874).

wards find the effect of the ruling. Let AB in Fig. 76 represent any linear aperture, and let it receive plane waves perpendicularly to itself. All the secondary waves transmitted by the ether particles in AB in the perpendicular direction BC agree completely in phase, and therefore when they are all brought to a focus by a lens their resultant will attain its highest possible value. In a direction BP, making a very small angle with BC, the agreement in phase will be disturbed. Drop the perpendicular AD, and then if BD equal one or any whole number of wave-lengths, there will be equal numbers of secondary waves at opposite phase proceeding in the direction BP, which, when brought to a focus by the lens, will have as resultant nil. If, however, BD be not equal to any multiple of λ, the resultant of the secondary waves will have some value which may be obtained as follows. In the first place, the phase of the resultant will necessarily always correspond with the phase of the secondary wave which issues from the ether particle or element in the middle of the aperture. If E be an ether particle lying in the aperture and EF the wave transmitted by the element at E, it is necessary to find

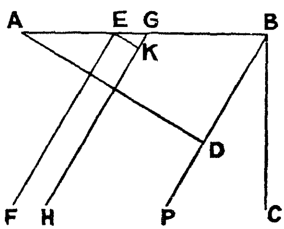


FIG. 76.

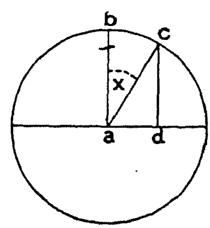


FIG. 77.

the disturbance produced at the focus of the lens by the elements lying along EA and EB; the sum of these will give the amplitude of the resultant at the lens focus. Consider the element at G, then clearly the secondary wave GH is retarded upon the wave EF by the amount GK, that is to say, the vibrations leaving G are a little later in phase than the vibrations simultaneously leaving E. Let the radius ab in Fig. 77 represent the amplitude of the vibration due to the wave from the element E, and the arc bc the short space of time the wave leaving the element G is behind this, then the perpendicular cd represents the amplitude of the vibration due to the element G. Let the angle $bac = x$, this being the angular retardation of the wave from the element G; now $cd = ab \cos x$, and, if the amplitude ab of the central wave be put equal to unity, $cd = \cos x$; that is to say, the amplitude of the vibration from the element G is equal to the cosine of the angular retardation. The amplitude of the resultant, therefore, at the focus of the lens, is equal to the sum of all the disturbances $\cos x \times \frac{dy}{\text{AB}}$ where $\frac{dy}{\text{AB}}$ is the ratio of the size of the element at G to the whole aperture AB.

Now if R be the angular retardation between the extreme waves from the elements at A and B, then clearly we shall have—

$$\frac{R}{AB} = \frac{x}{y},$$

when x is the relative angular retardation of two elements separated by a distance y.

By differentiation and rearrangement of terms—

$$\frac{dx}{R} = \frac{dy}{AB},$$

substituting $\frac{dx}{R}$ for $\frac{dy}{AB}$ in the expression for the amplitude, we see that the amplitude of the resultant is the sum of the disturbances $\cos x \times \frac{dx}{R}$.

Let E be considered as the centre of the aperture AB; then as R is the angular retardation between the waves from the extreme elements at A and B, $\frac{R}{2}$ is the angular retardation between the element at A and B respectively and the element at E. It follows that, considering the elements lying on each side of the central one at E, x must increase as one gets further from E, until it reaches $\frac{R}{2}$ on one side and $-\frac{R}{2}$ on the other side. In order to find the amplitude of the resultant vibration at the focus of the lens, it is therefore necessary to sum all the disturbances $\cos x\ dx \div R$, when x has all possible values between $-\frac{R}{2}$ and $+\frac{R}{2}$. The resultant amplitude is, therefore, given by $\int_{-\frac{R}{2}}^{+\frac{R}{2}} \cos x\ dx \div R$ if the amplitude in the principal direction BC $= 1$. This expression on integration $= \sin\frac{R}{2} \div \frac{R}{2}$, which is the amplitude required.

Considering the interference bands produced by such an aperture AB, the intensity of the central image when $R = 0$ is equal to unity; the first minimum corresponds to the condition that BD $= \lambda$, that is to say, that $R = 9\pi$, when the resultant amplitude is zero. The first maximum obtains when BD $= \frac{3}{2}\lambda$ and $R = 3\pi$; the amplitude is then equal to $\frac{2}{3\pi}$, and the intensity to $\left(\frac{2}{3\pi}\right)^2$. For the second minimum $R = 4\pi$, and thus the amplitude is again zero; similarly the second and third, etc., maxima have an intensity of $\left(\frac{2}{5\pi}\right)^2$, $\left(\frac{2}{7\pi}\right)^2$, etc. It is evident that the illumination falls off very rapidly on each side of the central image; for example, if AB be 25 mm. and λ be 5000 A., the angle θ corresponding to the first minimum (BD = 5000 A.) will be about 4″.

The effect of the ruling may be examined, and let us suppose the grating to consist of transparent bars of width a, alternating with opaque bars of width d. In the principal direction BC, the secondary waves are, of course, in complete agreement of phase, but their amplitude is diminished in the ratio of a to $a + d$. The central image of a line of light obtained with a grating is the same as if the rulings were absent, with the exception that the intensity is less in the ratio of a^2 to $(a + d)^2$. As regards the maxima on each side of the central image, these occur when the retardation between corresponding waves from adjacent apertures is equal to any multiple of λ, that is, when BD in Fig. 77 is equal to $mn\lambda$, when n equals the number of the maximum counting from the centre (the order of spectrum), and m the number of apertures. On either side of the maxima the illumination is distributed according to the same law as for the central image, and vanishes when the retardation amounts to $mn\lambda = \lambda$.

In considering the brightness of the maxima the effect of each aperture of the grating is the same. When the aperture AB was plain and had no rulings the angular retardation R between the two extreme elements was equal to $2\pi\frac{z}{\lambda}$, where $z =$ BD, the projection of the aperture upon the direction BC; in the present case R becomes equal to $2\pi\frac{az}{(a + d)\lambda} = \frac{2an\pi}{a + d}$ where $n = \frac{z}{\lambda} =$ order of spectrum. Substituting this value for R in the integral deduced above, we have for the ratio of brightness—

$$B_n : B_0 = \left(\int_{-\frac{an\pi}{a+d}}^{+\frac{an\pi}{a+d}} \cos x dx \div \frac{2an\pi}{a + d}\right)^2$$

$$= \left(\frac{a + d}{an\pi}\right) \sin_2 \frac{an\pi}{a + d},$$

where B_n and B_0 are the brightness of the nth spectrum and of the central image respectively.

If B represents the brightness of the central image when the whole of the grating aperture is transparent,

then $$B_0 : B = a^2 : (a + d)^2$$

and $$B_n : B = \frac{1}{n^2\pi^2} \sin^2 \frac{an\pi}{a + d}.$$

As the sine of an angle can never be greater than unity, it follows that under the most favourable circumstances only $\frac{1}{n^2\pi^2}$ of the original light can be obtained in the nth spectrum. If now $a = d$, then the formula becomes—

$$B_n : B = \frac{1}{n^2\pi^2} \sin^2 n\frac{\pi}{2};$$

so that when n is even, B_n vanishes, and when n is odd, $B_n : B = \frac{1}{n^2\pi^2}$. Under these circumstances the first order spectrum has an intensity of about $\frac{1}{10}$ of the original light, the second is wanting, and the third $\frac{1}{90}$ of the original. In general it is clear that the brightness of a spectrum vanishes when $\sin \frac{an\pi}{a+d} = 0$, which is the case when $\frac{an\pi}{a+d} = \pi, 2\pi, 3\pi$, etc. The spectra will therefore vanish for which $n = \frac{a+d}{a}, 2\frac{a+d}{a}, 3\frac{a+d}{a}$, etc. If, for example, $a = \frac{1}{4}d = \frac{1}{5}(a+d)$, then the 5th, 10th, 15th, etc., spectra will be wanting. Finally, if a be small compared with $a + d$, then, except for the higher orders, the above expression may be simplified to—

$$B_n : B = \left(\frac{a}{a+d}\right)^2,$$

that is to say, the brightness of all the spectra is the same.

The above equations show that in no case can the brightness of a spectrum exceed that of the central image; it must be remembered, however, that this result depends upon the hypothesis that the lines of the grating act by opacity, which in practice is very far from being true. In an engraved grating there is no opaque material present by which light can be absorbed, and therefore the effect depends upon the difference of retardation due to the alternate parts. If, for example, a grating were composed of equal alternate parts, both alike transparent but giving a relative retardation of half a wave-length, the central image would entirely be extinguished, while the first spectrum would be four times as bright as if the alternate parts were opaque. In the case of metal gratings the case is similar, and effects are produced by the reflections from the grooves, so that the character of the latter has great influence.

Rowland[1] has obtained an expression for the brightness of the lines of the spectra, which shows that the intensity is a function of λ as well as of n, so that the distribution of intensity in any grating spectrum may vary with the wave-length, and the sum of all the light in any one spectrum of a white source need not be equal to white light. On the basis of this work he was able to explain the fact, often observed, of the concentration of light into one spectrum to the detriment of the others, and also the excessive brightness of one particular colour in one spectrum. Rowland points out that if the diamond makes a single groove the lower orders will be the brightest, but if it rules several lines at once then the higher orders can be brighter. Asymmetry in the ruling produces asymmetry in the spectra.

It will generally be found, therefore, that a grating gives unequal

[1] "Gratings in Theory and Practice," *Astronomy and Astrophysics*, 12, 129 (1893).

spectra, that is to say, certain spectra brighter than others; very often this is noticeable on comparing the spectra obtained on each side of the normal.

It is important also to notice that the resolving power of a grating depends upon the accuracy of the ruling, which must be very high in order to ensure good results. For example, Rayleigh[1] compares two gratings which have the same amount of ruled space, but one with 1000 lines and the other with 1001 lines. Since the wave-lengths of the two D lines are practically different by a thousandth part, it is evident that the first grating would produce the same deviation for the D_1 line as the second grating would for D_2. If now the two gratings were combined to form one, the D lines would not be resolved, so that in a grating which is required to resolve the D lines there must be no *systematic* irregularity to the extent of a thousandth part of the grating space, though single lines may be out of position to a much larger amount. In a later paper[2] Rayleigh says, "It can make but little difference in the principal direction corresponding to the first spectrum, provided each line lies within a quarter of an interval from its theoretical position. But to obtain an equally good result in the nth spectrum, the error must be less than $\frac{1}{n}$th of this amount. It must not, however, be supposed that errors of this magnitude are unobjectionable in all cases. The position of the middle of the bright band representative of a mathematical line can be fixed with a spider line micrometer within a small fraction of the width of the band, just as the accuracy of astronomical observations far transcends the separating power of the instrument."

As regards the effect produced by errors of ruling, those arising from periodic errors may be mentioned. By periodic errors is meant the continual repeating of some false ruling; this usually arises from some defect in the ruling machine, which occurs at every revolution of the screw. The effect of errors of this kind is to produce false images of lines, which are called "ghosts." With a good grating these ghosts are often non-existent, but they may in cases assert themselves so much as to render a grating useless. It is the bright lines which most readily, of course, give rise to ghosts, and the latter may be recognised by their appearing as weak lines symmetrically placed on each side of the brighter lines. Rowland[3] has investigated the general theory of the effect of errors in the ruling of gratings; as regards the ghosts arising from periodic errors, he found that the intensity of the ghosts of the first order is proportional to the square of the order of the spectrum considered, and to the square of the relative variation from the true grating interval. Small spacing errors produce diffused light about the spectrum lines, which is taken from the lines themselves (*cf.* Bell, *vide* p. 33), and its amount is proportional to the square of the relative spacing error and

[1] *Phil. Mag.* (4), 47, 193 (1874).
[2] *Encyclop. Britt.*, 9th ed., **24**. Article: "Wave Theory," p. 438.
[3] *Loc. cit.*

the square of the spectrum order. A periodic error takes a certain quantity of light from the principal lines and distributes it symmetrically as a system of lines. The intensity of the ghosts and of the diffused light rapidly increases with the order of the spectrum. Rowland has calculated the relative brightness in three cases of the first order ghosts, which are as follows :—

Relative error.	Relative brightness of ghosts in—		
	First order.	Second order.	Third order.
$\frac{1}{25}$	$\frac{1}{63}$	$\frac{1}{16}$	$\frac{1}{7}$
$\frac{1}{50}$	$\frac{1}{252}$	$\frac{1}{63}$	$\frac{1}{28}$
$\frac{1}{100}$	$\frac{1}{1008}$	$\frac{1}{252}$	$\frac{1}{112}$

In the first column is given the relative error, that is to say the relation between the irregular spacing and the correct spacing. It will be seen that in the first case very strong lines will give visible ghosts in the first order, whilst in the third order the ghosts will have as much as one-seventh of the brightness of the principal lines—enough, perhaps, to render the grating useless. In the second case the ghosts will be visible in the third order, and barely so in the second; whilst in the third case the ghosts will not be visible in the first three orders.

The Concave Grating.—This type of grating was first produced by Rowland in 1882, and consists of a grating ruled upon a polished spherically concave surface of speculum metal, the rulings being equally spaced upon the chord of the arc, not upon the arc itself. It was found that, in the case of such a grating, if the grating and slit are placed upon the circumference of a circle which has as radius half the radius of curvature of the grating, the spectra are also focussed round the circumference. There is thus no need for lenses with these gratings—a fact which at once shows their immense superiority over the ordinary plane gratings. Indeed, there is little doubt that this grating has proved to be one of the finest spectroscopic machines ever produced.

Theory of the Concave Grating.—For the complete theory of the concave grating some larger text-book must be consulted, for it is too mathematical to find a place here. Certain theoretical points in connection with the practical working may be given. In the first place, to find the focal curve.

Let AB in Fig. 78 be a single element on a curved grating, XY; and let P be a point emitting light. PA and PB represent rays incident upon the element AB, making an angle of incidence i with the normal. These rays are therefore diffracted, and are focussed at the point Q, making an angle of diffraction θ. By the general grating equation we have, if AB is put as usual $= b$, $n\lambda = b(\sin i - \sin \theta)$; sin θ being negative because P and Q are on opposite sides of the normal. Let AC and BC be the normals at A and B; these will meet at the point C, which is the centre of curvature of the grating.

Considering the two rays PA and PB, these are incident at angles i and $i + di$, that is to say, the angles PAC, PBC are equal to i and $i + di$ respectively; similarly the two angles of diffraction QAC, QBC are equal to θ and $\theta + d\theta$ respectively. Let us further denote the angles at P, C, and Q by the letters x, y, and z, then in the two triangles PAE and CBE $x + i = y + i + di$, and similarly in the triangles CAF, QBF $y + \theta = z + \theta + d\theta$,

therefore $$di = x - y$$
and $$d\theta = y - z.$$

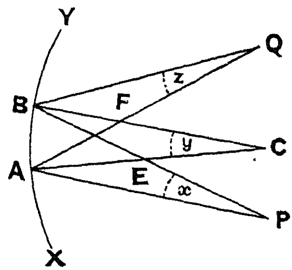


FIG. 78.

Now, if the light from P be homogeneous, it will be seen that, since Q is the focus of the diffracted rays from P, $\sin i - \sin\theta$ in the equation $n\lambda = b(\sin i - \sin\theta)$ is a constant; by differentiation, therefore—

$$\cos i di - \cos\theta d\theta = 0.$$

By substitution of the values found above for di and $d\theta$, we have—

$$\cos i(x - y) - \cos\theta(y - z) = 0.$$

By putting AP $= r$, AC $= \rho$, AQ $= s$, and AB $= b$, we have—

$$x = \frac{b}{r}\cos i,\ y = \frac{b}{\rho}\text{ and } z = \frac{b}{s}\cos\theta.$$

By substitution of these values in the last equation we have—

$$\cos i\left(\frac{b\cos i}{r} - \frac{b}{\rho}\right) - \cos\theta\left(\frac{b}{\rho} - \frac{b\cos\theta}{s}\right) = 0;$$

multiplying out and dividing throughout by b—

$$\frac{\cos^2 i}{r} - \frac{\cos i}{\rho} - \frac{\cos\theta}{\rho} + \frac{\cos^2\theta}{s} = 0,$$

whence $$s = \frac{r\rho\cos^2\theta}{r(\cos i + \cos\theta) - \rho\cos^2 i}.$$

Now, the distance r and the angle i are the polar co-ordinates of the point P, and similarly s and θ are the polar co-ordinates of the point

Q, so that if the point P move along any curve, the point Q will correspondingly move along another curve defined by this equation. The curve described by Q is, of course, the focal curve of the grating. If, now, P always move round a circle having a diameter equal to ρ, then of course—

$$r = \rho \cos i.$$

Substituting this value of r in the last equation we have—

$$s = \rho \cos \theta,$$

that is to say, the point Q will also move upon a circle with diameter equal to ρ. In other words, when the source of light and the grating are placed upon the circumference of the circle described with the radius

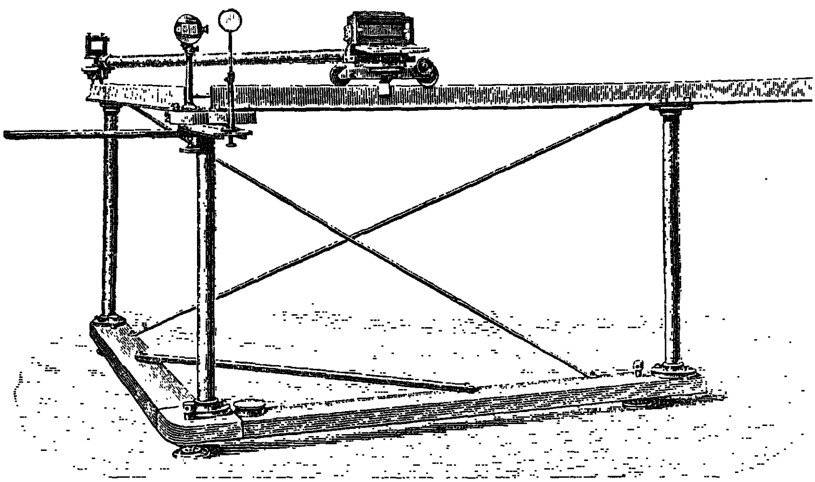


FIG. 79.

of curvature of the grating as diameter, the spectrum will always be brought to a focus upon that circle.

In mounting a concave grating it is necessary that this condition be fulfilled, and Rowland's method was described in Chap. II., p. 28. The mounting of a small grating is shown in Fig. 79.

Let us consider again the wave-length equation—

$$n\lambda = b(\sin i + \sin \theta).$$

We may substitute for θ the equivalent ratio $\frac{p}{\rho}$, where p is the length of arc of the focus circle corresponding to the angle of diffraction θ, and ρ is the radius of curvature of the grating,

therefore $$n\lambda = b \sin i + b \sin \frac{p}{\rho}.$$

Differentiating, sin i being constant,

$$n d\lambda = \frac{b}{\rho} \cos\frac{p}{\rho} dp$$

$$\frac{dp}{d\lambda} = \frac{n\rho}{b \cos\frac{p}{\rho}}.$$

This shows us that $\frac{dp}{d\lambda}$, or what may be called the linear dispersion of the spectrum, is, at any given position of the instrument, proportional to n, or the order of the spectrum. This is only another way of expressing the fact that the various orders of spectra are superposed, each superposed wave-length being inversely proportional to its order. This has already been proved before. Furthermore, the equation shows that the dispersion is a minimum when $p = 0$, *i.e.* at the centre of curvature of the grating; the linear dispersion is then equal to $\frac{n\rho}{b}$, and is constant; that is to say, the spectrum is normal at this point. It is possible to give p quite a large value and still find the spectrum normal, and it has been proved [1] that the error in normality is equal to $\frac{bp^3}{24n\rho^3}$; the error is therefore proportional to the cube of the linear distance from the centre of the photographic plate. An example may be given of this. In the case of the largest Rowland concave grating at present in the market, $b = 0{\cdot}000127$ cm. and $\rho = 650$ cm., and putting the maximum allowable error at $\frac{1}{1000}$ Ångström, then we have ($n = 1$)—

$$p^3 = \frac{1 \times 10^{-11} \times 24 \times (650)^3}{0{\cdot}000127}$$

and $p = 8$ cm. nearly.

It is, therefore, possible to photograph 16 cm. of the first order spectrum (8 cm. on each side of the centre) perfectly normal within this error, which is, in fact, the greatest attainable accuracy with our present measuring apparatus.

Similarly, it can be found that with the same grating the deviation from normality at the ends of a 50 cm. photograph is only 0·03 A. in the first order. The distances are closely proportional to these with the smaller gratings, as may readily be found from the above expression.

If now we consider the spectra produced at the centre of curvature of the grating, *i.e.* when $\theta = 0$, we have—

$$n\lambda = b \sin i,$$

and

$$\sin i = \frac{n\lambda}{b}.$$

But the distance from slit to eyepiece (AE in Fig. 15, p. 29) is equal to

[1] Kayser, *Handbuch der Spectroscopie*, i. 466.

$\rho \sin i$, and if ρ again be put equal to the radius of curvature, this distance therefore $= \frac{\rho n \lambda}{b}$, that is to say, in any given order it is directly proportional to the wave-length. It is possible, therefore, to mark off on the grating rail a linear scale on which the wave-lengths may be approximately read off from the position of the eyepiece. It is important to notice that this scale is the same as the normal scale of the spectrum obtained upon the photographic plate at the centre of curvature; for if the distance from slit to eyepiece be put $= g$, then $\frac{dg}{d\lambda} = \frac{\rho n}{b}$, which is the value of the linear dispersion upon the photographic plate $\frac{\rho n}{b \cos \frac{p}{\rho}}$, when $\cos \frac{p}{\rho} = \cos \theta = 1$, *i.e.* when $\theta = 0$. This constant $\frac{\rho n}{b}$ is called the scale of the instrument, and for the largest gratings of 650 cm. focus and 20,000 lines to the inch it is equal to 5,118,100 in the first order; a change in wave-length of 1 A. means therefore a change of position on the plate of about 0·5 mm. in the first order, and n times this in the nth order. It follows from this, and what has gone before, that it is possible with Rowland's largest gratings to photograph upon one plate a range of 320 A. normally, with a maximum error of $\frac{1}{1000}$ A.

It may again be pointed out here that this scale is perfectly constant over the whole range of the instrument, so that all photographs taken with it are absolutely comparable with one another, a fact which alone upholds the immense superiority of the concave grating over any other spectroscopic instrument.

It must not be forgotten that this method of mounting puts a limit upon the spectra which can be observed. As a general rule, the largest workable value of the angle of incidence is about 70°; above this the angular aperture of the grating falls so rapidly as materially to decrease the illumination. We have, therefore—

$$n\lambda = b \sin 70°,$$

and

$$\lambda = \frac{0{\cdot}94 b}{n}.$$

The practical maximum value of λ in the first order with a 20,000 line grating is about 12,000 A.; in the second order, 6000 A.; in the third, 4000, and so on. With a 10,000 line grating the practical limits will be twice the above.

It is thus necessary, in working with rays of great wave-length, to make use of gratings ruled with comparatively few lines to the inch; it is preferable, on the other hand, to use closely ruled gratings when work is to be done upon the ultra-violet spectra, since it is in this way possible to get greater resolving power in the first order, the first order being dealt with on account of the greater freedom occurring here from overlapping of the higher orders.

We have, lastly, to deal with the astigmatism of the concave grating. Since the grating in Rowland's mounting is always more or less obliquely situated with regard to the incident light, the spectrum obtained from a point source of light is always more or less widened out, so that a spectrum of lines of greater or less length is obtained with a point as the light source. The greater the obliquity—that is to say, the greater the angle of incidence—the more pronounced is the widening. This widening is parallel to the rulings of the grating, and depends upon their length and upon the angle of incidence. It has been shown [1] that the length of the lines when a point source is used is equal to—

$$\sin i \,.\, \tan i \,.\, l,$$

where l is the length of the rulings on the gratings. In the case of Rowland's largest grating $l = 5$ cm., the length, therefore, of a line at 6000 A., given in the first order, with a point source, is $0{\cdot}25l = 1{\cdot}25$ cm., since the angle i would be $28^\circ\ 12'$. If a slit be used as the source of light, every point will be drawn out into a line, and these linear images overlapping one another give a line considerably longer than the original slit. Kayser gives as the length of the brightest portion of the spectrum lines—

$$\frac{s}{\cos i} - \sin i \,.\, \tan i \,.\, l,$$

and for the whole length of the lines—

$$\frac{s}{\cos i} + \sin i \,.\, \tan i \,.\, l,$$

where s is the length of the slit.

As a result of this astigmatism, "dust lines," which arise from the presence of particles of dust between the slit jaws, are not formed in the spectrum; these horizontal dust lines are brought to another focus.

This property of the concave grating renders it impossible to obtain two sharply defined adjacent spectra for comparison by means of the draw slides upon the slit, or a comparison prism, as described upon p. 46, for prism apparatus. For such comparison a mechanical method is usually used (*vide infra*, p. 185). Sirks,[2] however, has shown that a comparison prism can be used if it be placed a certain distance away from the slit. This may be seen from Fig. 80, where G is a grating with a radius of curvature equal to GC; the slit is at A, and the incidence angle i = AGC. A beam of light is shown coming from PP, passing through the slit at A, and focussed by the grating G at C. Now the slit A produces a vertical image at C, and there is also a horizontal focus line at EF, so that a horizontal wire stretched across the incidental beam of light at EF will be focussed as a horizontal line on the plate at C. It therefore follows that if a very narrow right-angle prism be placed

[1] Kayser, *Handbuch der Spectroscopie*, i. 463.
[2] Sirks, *Astronomy and Astrophysics*, 13, 763 (1894).

horizontally at EF, a sharply defined narrow horizontal strip will be cut out of the centre of the spectrum at C. A second source of light can be thrown in through this prism, with the result that the chief spectrum at C will have a narrow and sharply defined comparison spectrum running horizontally along its centre. It is clear that the size of the prism and its distance from the slit varies with every position of C; these may readily be calculated. First, the distance DA—

$$DA = DG - AG;$$

now $$DG = \frac{\rho}{\cos i}, \text{ where } \rho \text{ as usual } = GC$$

and $$AG = \rho \cos i,$$

therefore $$DA = \frac{\rho}{\cos i} - \rho \cos i = \rho \sin i \tan i.$$

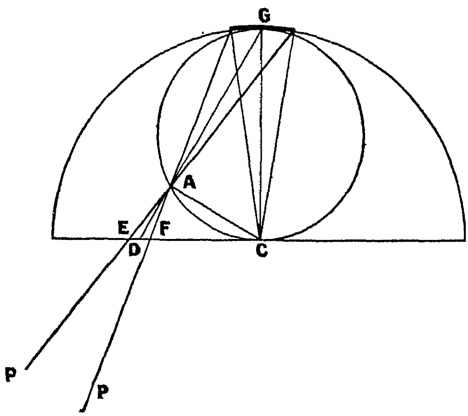


FIG. 80.

Secondly, the length of face EF. If the total width of the grating be $= d$, then—

$$\frac{EF}{d} = \frac{DA}{AG}$$

and $$EF = \frac{\rho d \sin i \tan i}{\rho \cos i}$$
$$= d \tan^2 i.$$

The Concave Grating, Eagle's Mounting.—As was briefly explained on page 35, the coincidence method of wave-length measurements with concave gratings as used by Rowland has been found to be inaccurate, and consequently one of the great advantages of the Rowland method of mounting has disappeared, with the result that the disadvantages become more pronounced. This method has now been almost entirely superseded by the Eagle mounting, in which the greater advantages over the older method more than counterbalance the

inconveniences. The Eagle mounting will be described in detail in the next chapter and it is only necessary to make brief reference to it here. It is of the Littrow type, that is to say, the incident and diffracted rays make almost the same angle with the normal, and therefore the condition of minimum deviation is secured. Under these conditions the definition is the best possible, but of course the spectra obtained are not normal since the wave-length is found from the equation (see p. 31)—

$$n\lambda = 2b\left(\sin\frac{\phi}{2}\right).$$

The general condition laid down above is secured in this mounting, namely, that the eyepiece or photographic plate, the slit, and the grating lie on the circumference of the circle having the radius of curvature as diameter, but the focus is not automatically maintained as in Rowland's method. These are the two principal disadvantages of the Eagle mounting, but, as will be fully explained in the next chapter, they are not so great as might at first be thought.[1]

One of the great advantages of the Eagle mounting may be mentioned here, since this is concerned with the general theory of the concave grating. The astigmatism is very much less than with the Rowland mounting, and as the astigmatism necessarily means loss of light, the advantage gained is great compared with the Rowland mounting, where the loss of light, especially in the higher orders, is very considerable. As shown above, with Rowland's mounting the length of the line given by a point source is $\sin i \,.\, \tan i \,.\, l$, where l is the length of the grating rulings. Eagle shows that with his mounting the length of the line given by a point source is $2l \sin i$. The following table gives a comparison of the angles of incidence and the astigmatism for $\lambda = 5500$ in the first five orders with a grating of 15,020 lines to the inch:—

Order.	Rowland's mounting.		Eagle's mounting.	
	Angle of incidence.	Astigmatism.	Angle of incidence.	Astigmatism.
First . . .	18° 59′	$0{\cdot}112l$	9° 22′	$0{\cdot}053l$
Second . . .	40° 35′	$0{\cdot}557l$	18° 59′	$0{\cdot}212l$
Third . . .	77° 20′	$4{\cdot}34l$	29° 12′	$0{\cdot}476l$
Fourth . . .	Impossible	—	40° 35′	$0{\cdot}876l$
Fifth . . .	Impossible	—	54° 23′	$1{\cdot}321l$

From this table it may be seen how great is the gain in brightness secured in the higher orders with the Eagle mounting as compared with the Rowland mounting.

Until fairly recently the only gratings obtainable were those ruled on one of the two ruling machines constructed by Rowland. Some

[1] *Astrophys. Journ.*, 31, 120 (1910).

years ago the late Lord Blythswood, with the help of the late Mr. Otto Hilger, made a grating-ruling engine which has been deposited by Lady Blythswood in the custody of the National Physical Laboratory.[1] This machine has been slightly modified and is now in good order, and gratings ruled thereby can be purchased. The main screw of the instrument has 20 threads to the inch and is fitted to a large wheel with 720 teeth. As at present arranged, therefore, the maximum number of lines that can be ruled is 14,400 to the inch. Very accurate mechanical adjustments are employed to avoid the occurrence of periodic errors in the ruling, and in order to maintain a constant temperature the whole machine is mounted in a heavily lagged case; within this case is a thermostat of the Goüy type by means of which the temperature is kept constant during the ruling to 0·01° C. Vibration is minimised as far as possible by mounting the machine on a very massive foundation and, further, the actual ruling is done very slowly. The average rate is about 4 lines a minute, so that a 6-inch ruled surface, containing 86,400 lines, takes about a fortnight to complete.

It is possible by moving the toothed wheel two, three, or four teeth at a time to rule gratings with 7200, 4800, or 3600 lines to the inch. It is proposed to adapt the machine with the view of ruling 28,800 lines to the inch. As regards quality, the gratings produced by this machine are excellent, being quite as good as those ruled by the Rowland engines.

The Michelson Echelon Diffraction Grating.—This grating was designed by Michelson with the view of obtaining an instrument of very high resolving power, which, at the same time, would give spectra of great brilliancy. In the case of the ordinary diffraction grating, the illumination falls off very rapidly as one mounts into the higher orders; the resolving power is very great with the echelon, because the relative retardation between the extreme rays entering the telescope is very great indeed, and, just as in the ruled grating, the resolving power may be said to depend upon the retardation between the rays from the extreme apertures.

The echelon grating is made by setting together a series of perfectly parallel glass plates of equal thickness, which decrease in size by an equal amount, as is shown in Fig. 81. The beam of parallel light is incident normally on the top plate in the diagram, and the rays, after passing through, are brought to a focus by a lens. The pencils *a*, *b*, *c*, etc., coming from the different elements of the grating are retarded upon one another by reason of the difference in the velocity of the light through the glass and air, and thus interference is set up at the focus of the lens, and a spectrum is produced. It will be seen that the relative retardation between the rays from the two extreme elements is very great, and therefore the order of spectrum obtainable is very high; and since the direction in which the spectra are obtained is in the direction of propagation of the light, the brightness of these spectra is very considerable.

[1] National Physical Laboratory, Descriptive Notes on the Metrology Department, March, 1921.

Dispersion.—The analytical expressions for the production of the spectra are readily obtained, as may be seen from Fig. 82, where only two adjacent apertures are drawn, which are quite sufficient for the purpose.

Let $ab = s$ be the breadth of an aperture, and $bd = t$ the thickness of each plate. The angle of diffraction, θ, of the spectra observed is very small, and if p be the order of the spectrum observed, then the relative retardation of the rays of two interfering pencils will be equal to $p\lambda$. Evidently, therefore, the relative retardation between the rays leaving a and d must be equal to $p\lambda$, and, therefore, we may put—

$$p\lambda = nbd - ae = nt - ae,$$

where n represents the index of refraction of the glass for wave-length λ, *i.e.* the relative velocity in air and glass.

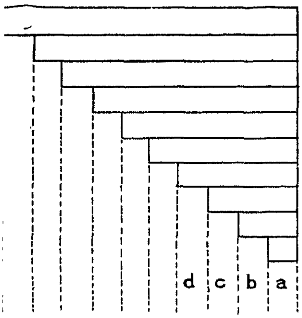


FIG. 81.

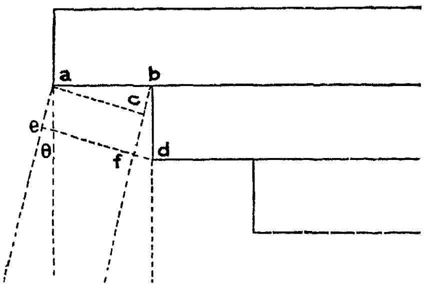


FIG. 82.

Now $\qquad ae = bf - bc = bd \cos\theta - ab \sin\theta$

therefore $\qquad p\lambda = nt - t\cos\theta + s\sin\theta.$

But θ is extremely small, so that $\cos\theta$ may be put $= 1$ and $\sin\theta = \theta$, and thus we have—

$$p\lambda = (n - 1)t + s\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By differentiation with respect to λ, n being constant—

$$pd\lambda = tdn + sd\theta$$

and $$\frac{d\theta}{d\lambda} = \frac{1}{s}\left(p - t\frac{dn}{d\lambda}\right).$$

Substituting for p its approximate value $\frac{(n - 1)t}{\lambda}$, from (1) (θ being extremely small), we have—

$$\frac{d\theta}{d\lambda} = \frac{t}{s\lambda}\left[(n - 1) - \lambda\frac{dn}{d\lambda}\right]$$

$$= \frac{bt}{s\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where b represents the coefficient within the square brackets, which, it will be noticed, is entirely a function of the glass employed, and may be calculated from its optical constants. It lies between 0·5 and 1·0 for most glasses.

Equation (2) gives the dispersion of an echelon grating, and shows that the dispersion of a grating of a given glass for light of a given wave-length is independent of the number of steps, and varies directly as the thickness of the plates, and inversely as the breadth of aperture of each element.

By differentiation of equation (1) with respect to p keeping λ constant—

$$\lambda dp = s d\theta$$

and
$$\frac{d\theta}{dp} = \frac{\lambda}{s};$$

putting
$$dp = 1$$

then
$$d\theta_2 = \frac{\lambda}{s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $d\theta_2$ is the change in deviation occurring in passing from one order to the next; that is to say, the angle between the images of the same line in two consecutive orders is equal to $\frac{\lambda}{s}$. This separation of orders is, therefore, only dependent upon the wave-length and the width of step.

Resolving Power.—If $d\theta_3$ represent the angular limit of resolution, that is to say, the angular separation of two lines which are just seen separated in the telescope, then (*vide* p. 65)—

$$d\theta_3 = \frac{\lambda}{a}$$

where a is the effective aperture of the telescope object glass; but this is equal to the sum of the width of all the steps $= ms$, m being the number of elements;

therefore
$$d\theta_3 = \frac{\lambda}{ms} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By substitution of this value of $d\theta$ in equation (2),

we have
$$\frac{\lambda}{d\lambda} = r = \frac{bmt}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

The resolving power of an echelon grating is thus proportional to the total thickness of glass traversed, and for a given wave-length is independent of the thickness of the plates or width of the steps.

A comparison of equations (3) and (4) shows that the angular limit of resolution is $\frac{1}{m}$th of the angular separation of two consecutive orders.

The Intensity of Illumination.—Evidently this is a maximum when $\theta = 0$, because this is the principal direction of propagation of the light; if this be put equal to unity, the intensity in oblique directions will be found from the expression—

$$I = \frac{\sin^2 \pi \frac{s}{\lambda} \theta}{\left(\pi \frac{s}{\lambda} \theta\right)^2}$$

which is deduced in exactly the same way as the similar expression on p. 157. From this it is evident that the illumination vanishes when $\theta = \frac{\lambda}{s}$; but by equation (3) the angle between the images of the same line in two consecutive orders is also $= \frac{\lambda}{s}$. If, therefore, a line be obtained in the position $\theta = 0$, the images of the same line in the next lower and the next higher orders will vanish.

As an example of the application of the above formulæ, an echelon made by Hilger may be chosen. For this instrument the [illegible] constants were—

$$t = 10 \text{ mm.}$$
$$s = 1 \text{ mm.}$$
$$\text{number of plates} = 20;$$

optical constants—

$$\begin{aligned}
n_C &= 1{\cdot}5706 & \lambda &= 6{\cdot}5631 \times 10^{-5} \text{ cm.} \\
n_D &= 1{\cdot}5746 & \lambda &= 5{\cdot}8930 \times 10^{-5} \text{ cm. (mean of } D_1 \text{ and } D_2) \\
n_F &= 1{\cdot}5845 & \lambda &= 4{\cdot}8615 \times 10^{-5} \text{ cm.} \\
n_G &= 1{\cdot}5927 & \lambda &= 4{\cdot}3410 \times 10^{-5} \text{ cm.}
\end{aligned}$$

The value of $\frac{dn}{d\lambda}$ for this glass at $\lambda = 5{\cdot}8930 \times 10^{-5}$ as calculated from Cauchy's formula as shown on page 62 is $- 7113$ by interpolation between n_C and n_F. Substituting this and the values of n_D and λ for the D line in the coefficient $(n - 1) - \lambda\frac{dn}{d\lambda}$, b_D is found to be equal to $0{\cdot}5746 + 0{\cdot}0419 = 0{\cdot}6165$.

Dispersion.—From equation (2)—

$$\frac{d\theta}{d\lambda} = \frac{bt}{s\lambda}$$

therefore $\qquad \frac{d\theta}{d\lambda} = 104{,}615$ at wave-length 5893 A.

putting $\qquad d\lambda = 0{\cdot}1 \text{ A.} = 1 \times 10^{-9}$ cm.

$$d\theta = 0{\cdot}0001046 \text{ radian}$$
$$= 22'' \text{ of arc.}$$

That is to say, that the angle between two rays which differ in wave-length by 0·1 A. is 22″ of arc.

Separation of Orders.—From equation (3)—

$$d\theta_2 = \frac{\lambda}{s} = 0{\cdot}0005983 \text{ radian}$$
$$= 2' \text{ of arc.}$$

This being the angle between the images of the same line in consecutive orders.

Angular Limit of Resolution.—From equation (4) this is $\frac{1}{m}$th of the separation of orders. Now the number of plates was twenty, but the aperture of the telescope object glass is 1 mm. larger than the largest plate, so the number of effective apertures is $21 = m$;

therefore $d\theta_3 = 6''$ nearly,

this being the angle between two rays in the neighbourhood of D which can just be seen separated. From equation (4*a*) the difference in wave-length of two such rays which can just be separated—

$$d\lambda = \frac{\lambda^2}{bmt} = \frac{5{\cdot}893^2 \times 10^{-10}}{0{\cdot}6165 \times 21 \times 1}$$
$$= 0{\cdot}027 \text{ Ångström.}$$

Therefore the instrument will resolve lines which differ in wave-length by 0·027 A.

Finally, the resolving power is equal to $\frac{bmt}{\lambda} = 218{,}330.$

In the modern form of the echelon, the plates, after having been thoroughly cleaned, are carefully clamped together and mounted on a stand, provided with levelling screws. It is hardly necessary to point out with what accuracy the plates must be worked, and with what care they must be handled. As usual with gratings, the plates are so mounted that the apertures are parallel to the slit. An echelon with thirty-two plates is shown in Fig. 83.

It is necessary in making use of an echelon grating that the light be submitted to a preliminary analysis, by means of a prism, before it is allowed to enter the echelon apparatus, on account of the very small angle between two successive orders of spectra. For this purpose the most convenient form of auxiliary spectroscope is the constant deviation instrument described on page 105. With this apparatus the eyepiece is removed, and the telescope object glass so adjusted as to focus the image of the slit upon the slit of the echelon instrument; by simply turning the constant deviation prism any desired line can be brought on the echelon slit, without any further adjustment. The echelon spectroscope is similar to any ordinary spectrometer, in that it possesses a collimator and telescope; it is, as will readily be seen from what has

gone before, essentially a direct-vision instrument; it should be provided with a centre table which can be rotated to a small extent, and, further, there should be an arrangement by means of which the echelon can be swung out of the field of view.

In Fig. 84 is shown an echelon spectroscope, with a constant deviation spectroscope for the preliminary analysis of the light. The echelon itself is at A, and the telescope and collimator at B and C respectively; the slit is shown at D. E is the constant deviation instrument, with its collimator and telescope; it will be noticed that the latter has no eyepiece, but is brought close up against the echelon slit, so that this slit may be in the focal plane of the telescope objective. All the necessary adjustments can be carried out from the eyepiece end of the echelon; the handle F regulates the echelon slit, the handle G rotates the constant deviation prism, whilst the handle H adjusts the echelon itself. The arrangement for swinging the echelon out of the field of view is not shown in the illustration; this is only used in the preliminary adjustments.

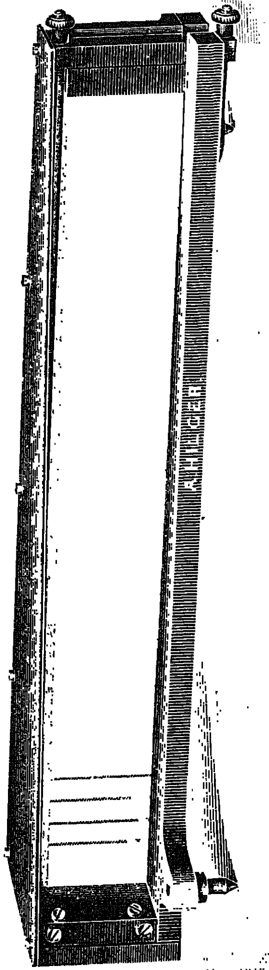


Fig. 83.

The adjustments of the apparatus are very simple and straightforward. In the first place, it is necessary to see that the telescope of the auxiliary spectroscope is in an exact straight line with the collimator and telescope of the echelon instrument; and in the second place, that the object glass of the auxiliary telescope correctly focusses the image of the slit upon the echelon slit. A sodium flame is then brought in front of the auxiliary slit, and the prism turned until the D lines are brought upon the echelon slit; on looking through the echelon telescope with the eyepiece removed, the object glass should appear equally illuminated all over, with, perhaps, two slight and symmetrical black strips to the right and left; if this is the case the instrument is in adjustment.

A line that it is required to examine may now be brought upon the

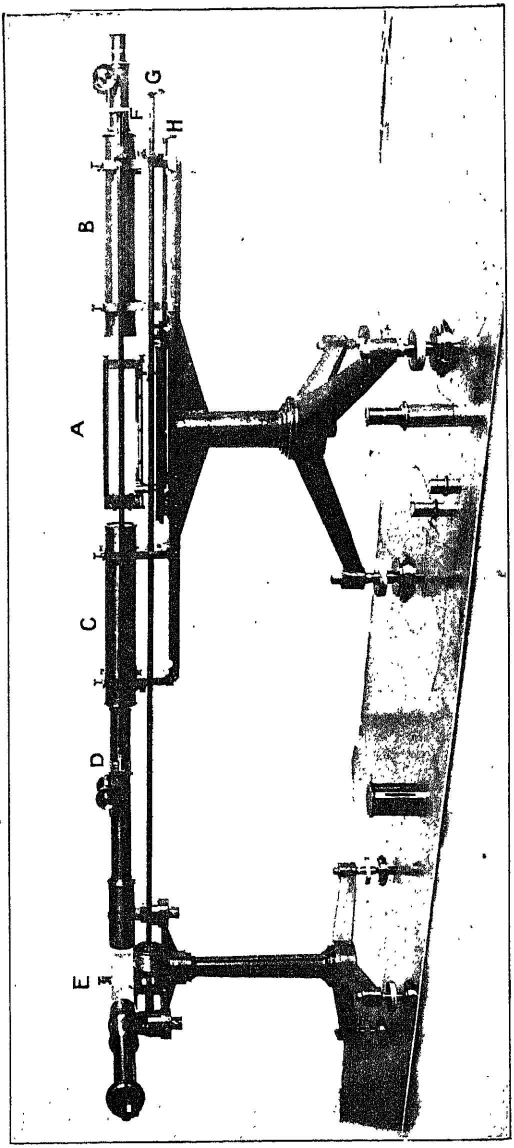


Fig. 84.

echelon slit, and, following on the theory given above, different phenomena may be seen on looking through the echelon telescope. For example, if the line be seen under the condition $\theta = 0$, then it will

appear as a single very bright line in the middle of the field, with a series of very faint lines diminishing in intensity on each side of it. The two neighbouring orders on each side are now absent $\left(\text{since } \theta = \frac{\lambda}{s}\right)$, and the faint lines are the next higher orders to these—very faint, because they are visible under larger values of θ. This condition may not be realised, and there may be seen two equally bright lines, which are two successive orders of the same line, and at the same time the series of faint lines on each side. Again, the condition may lie between the above two, so that two lines of unequal brightness are seen. It is important to notice that on each side of the centre of the field there is a dark point corresponding to the condition that $\theta = \frac{\lambda}{s}$; between these dark points is a region equivalent to twice the distance between two consecutive orders. It is this region that should be examined, and the fainter lines lying outside the two dark points will not in any way interfere. By a slight rotation of the echelon on its vertical axis any required condition can be obtained, and a number of orders can be made to cross the field of view. It will be found during the rotation of the echelon that there is one position at which the direction of motion of the lines in the field is reversed; the echelon is then normal to the incident light, which is the best position for work.

The chief objection to this grating lies in the small value of the separation of consecutive orders of spectra. The objectionable nature of this makes itself felt, when lines are examined which have a considerable breadth of their own. For example, in the case of the grating given above, the angular separation of consecutive orders is about 2′ of arc, or 0·0005893 radian, while the dispersion is 104615 at D, *i.e.* $d\theta_1 = 0{\cdot}0001046$ radian when $d\lambda_1 = 0{\cdot}1$ A. The greatest possible breadth, therefore, of a line in the neighbourhood of D which can be observed without two orders overlapping is about 0·56 A.

The Echelette Grating.—One of the most important problems connected with the grating is the question of the distribution of intensity amongst the spectra of the different orders. Practically no rigorous investigation has been made owing to the impossibility of determining the actual form of the groove in a ruled grating. Wood[1] has attacked the problem by making gratings with grooves of such large size as to make a determination of their exact form a matter of certainty, and then investigating the energy distribution by means of the long heat waves. By employing the residual rays from quartz as discovered by Rubens and a grating with say 1000 lines to the inch, it is evident that we should have about the same ratio of wave-length to grating space as in the case of a Rowland grating with 14,000 lines to the inch and red light. Thus gratings with constants varying from 0·1 mm. to 0·01 mm. could be studied by means of the residual rays or narrow regions of the infra-red spectrum isolated by means of a rock-salt prism.

[1] *Phil. Mag.*, **20**, 770 and 886 (1910).

Wood has succeeded in preparing such gratings, and it has been shown by him in conjunction with Trowbridge that they are singularly adapted for study of the infra-red spectrum. For by means of such gratings a much greater resolving power can be obtained than has hitherto been found possible for such long wave-lengths. It is found that in these gratings a larger percentage of the energy is thrown into the first or second spectra and thus they may be regarded as reflecting echelon gratings of comparatively small retarding power, and Wood has proposed the name of echelette, to distinguish them from the ordinary grating or the Michelson echelon. The method finally adopted for their manufacture was as follows: A sheet of polished copper plate such as is used by photo-engravers for the half-tone process was gold plated and polished. A carborundum crystal was used for the ruling point. The crystals were selected by breaking up the mass of the substance as it comes from the furnace, the natural edge of the crystals being so straight that they rule a groove with optically perfect sides. It is hardly necessary to point out that the success of the grating depends upon this fact. In the ruling everything depends on the nature of the edge and the angle at which the crystal is set, *i.e.* the tilt forwards or backwards with respect to the direction of the ruling. When the ruling is properly carried out the groove is formed simply by a compression of the gold surface, no metal being removed. Since the angle of the carborundum crystal is 120° the sides of the groove approximately enclose this angle, and according to the position of the crystal so the grooves may be obtained of various shapes. The crystal is mounted so as to rule a groove with one edge at an angle of 20° or less with the original surface, and it is found that such a grating when illuminated with infra-red radiation of longer wave-length than say 3μ behaves like an ideal grating, and gives spectra similar to those given by an ordinary grating which throws practically all the light into one or two orders on each side of the central image.

A complete investigation of these gratings was commenced by Trowbridge and Wood,[1] the complete results of which, however, have not yet been published, but the investigation has been carried sufficiently far to indicate that the method gives reliable experimental data regarding the relation between the form of the groove and the distribution of energy. In practice it is found that owing to the diffraction of the radiation from the reflecting plane, it is not possible to concentrate all the energy into one single spectrum, but with a properly sloped edge as much as 70 per cent. of this can be utilised.

The application of these gratings to the study of radiations such as the residual rays of quartz is described by Trowbridge and Wood[2] in a third paper, and their superiority in resolving power as compared with a rock-salt prism is manifest; for example, the quartz residual rays which Coblentz found to consist of two closely situated maxima at $8{\cdot}5\mu$ and 9μ were now found to consist of two maxima of equal intensity at $8{\cdot}41\mu$ and $8{\cdot}90\mu$ sharply separated by a minimum with an intensity of one-

[1] *Phil. Mag.*, **20**, 886 (1910). [2] *Ibid.*, 898 (1910).

third that of the maxima. This minimum is therefore very much more pronounced than appears from Coblentz's method. Similarly, in the case of the carbon dioxide radiation from the bunsen burner the radiation at $4{\cdot}4\mu$ is undoubtedly resolvable into two maxima at $4{\cdot}3\mu$ and $4{\cdot}43\mu$ respectively. The dispersion of these gratings has been compared with that of rock-salt and fluorite prisms, and it has been found that between 4μ and 5μ it is nearly 17 times that of a 60° rock-salt prism and 4 times that of a fluorite one. Between 8μ and 9μ the echelette grating has a dispersion of 5·4 times that of the rock-salt prism. The grating space of the grating used was 0·0123 mm.

CHAPTER VII.

THE RULED GRATING IN PRACTICE.

The Plane Grating.—As already described in the introduction (p. 31), there are several methods in which a plane grating may be used. Generally speaking, however, except in cases of absolute measurement, the plane grating is not so serviceable as the concave grating for wave-length determinations; recently by far the best absolute determinations have been made by the interference methods of Michelson, and of Fabry and Perot, so that a plane grating may be considered as of little use in accurate work. They still, however, find a use for ordinary work, especially the very excellent copies which may now be purchased very cheaply. The following directions are given as showing the methods of work with these instruments.

The general equation, as before stated, is—

$$n\lambda = b(\sin i + \sin \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\sin \theta$ is positive or negative according as the incident and diffracted rays are on the same or opposite sides of the normal. This equation can be written in the form—

$$n\lambda = 2b \sin \frac{i+\theta}{2} \cos \frac{i-\theta}{2};$$

and since $i + \theta$ is equal to the angle of deviation which may be called ϕ,

therefore $$n\lambda = 2b \sin \frac{\phi}{2} \cos \frac{i-\theta}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this equation it is clear that the larger the value of the term $\cos \frac{i-\theta}{2}$, the smaller the value of the term $\sin \frac{\phi}{2}$, and that when $\cos \frac{i-\theta}{2}$ has a maximum value, $\sin \frac{\phi}{2}$, and therefore the angle ϕ, will have a minimum value. The term $\cos \frac{i-\theta}{2}$ has a maximum value of 1 when $i - \theta = 0$, *i.e.* when $i = \theta$; it therefore follows that the deviation obtained with a grating is a minimum when the angles of incidence and diffraction are equal to one another, and that under these conditions the general wave-length equation is simplified to the form—

$$n\lambda = 2b \sin \frac{\phi}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the case of a transmission grating the condition of minimum deviation is readily enough obtained by so setting the grating that the incident and diffracted rays make equal angles with the normal. With a reflecting grating, however, minimum deviation can only be obtained in the Littrow type of apparatus, in which the incident and diffracted rays pass through the same telescope as in the Eagle mounting of the concave grating described on page 166.

The position of minimum deviation with a grating has a certain advantage in that the definition is always very much improved, but at the same time it is rather laborious in practical work with a plane grating. It was, however, used by Mascart in his determinations of absolute wave-length.

The above equations are sufficient for all the methods of measurement of wave-length with plane gratings. There are five of these methods, differing slightly from one another (*vide* p. 31). In the first two methods the grating is set perpendicularly to the collimator or the telescope, and thus in equation (1) either i or θ is made equal to zero, and so we may write the equation as—

$$n\lambda = b \sin \phi,$$

where ϕ is the angle of deviation.

In the third method the grating is not set perpendicularly to either the telescope or the collimator, and therefore equation (1) is applicable.

The fourth method is that of minimum deviation described above; and the fifth method is to fix the collimator and telescope firmly at some known angle to one another and to rotate the grating.

In equation (3) the term $i - \theta$ evidently represents the angle between the incident and diffracted rays, and thus the angle between the collimator and the telescope; if this be known, it will only be necessary to determine the value of ϕ or the deviation in order to find λ from equation (3).

In all cases of mounting plane gratings for purposes of measurement of wave-length, a spectrometer must be employed; for the first, second, and third methods the spectrometer must be provided with a rotating telescope, the amount of rotation of which can be measured, and the same for the fourth method with transmission gratings. With the fourth and fifth method, using reflecting gratings, a spectrometer table must be used, by means of which the necessary amount of rotation given to the grating can be measured.

In the first two methods, where the grating is set perpendicularly to the collimator and the telescope respectively, an ordinary spectrometer is employed such as was described for a prism on page 102; the adjustment of the apparatus as regards illumination is precisely the same as in the case of the simple prism apparatus; there is, however, in all cases of grating mounting an additional adjustment which must be attended to, namely, to see that the rulings on the grating are parallel to the slit, for otherwise the definition will be hopelessly ruined.

It is very convenient to have the grating mounted upon a table provided with three levelling screws, as this enables the necessary adjustments for verticality, etc., to be readily made. When a grating has been properly adjusted, the spectra should not rise or fall in the field of view of the telescope when the grating is rotated on its vertical axis.

If the first method of working be adopted, then, after all the preliminary adjustments have been satisfactorily made, the grating is turned until it is normal to the collimator. When this is the case the angle of deviation for any line will be the same on each side of the normal, and therefore the position of the grating may be tested in this way. In the case of a transmission grating, the cross-wire in the telescope eyepiece is first fixed upon the image of the slit obtained straight through the grating and the reading taken; the telescope is then turned until the image of some line is brought upon the cross-wire and the reading taken; the telescope is then turned back until the same line in the same order on the other side of the normal is brought upon the cross-wire. The two angles of deviation must be equal; if they are not, the grating is turned one way or the other until equal angles are obtained. When this is the case, the wave-lengths of any lines may be found from the equation $n\lambda = b \sin \phi$. In this way by taking readings on each side of the normal, greater accuracy is obtained. If a reflecting grating be used, it will, of course, be necessary to take the reading of the direct image before the grating is put in place; the deviation in this case will, of course, be the angle between the collimator and the telescope when fixed on the line in question, and will be equal to the difference between 180° and the angle through which the telescope is turned from the direct image to the line in question.

The second method is preferably restricted to reflecting gratings, and evidently in this case the grating must be so placed that the telescope, when fixed upon the line in question, bisects the angle between the incident rays from the collimator and the reflected rays. This method possesses the inconvenience that the grating must be adjusted for every line measured.

In the third method the grating is not necessarily placed in any particular position, but the angles of incidence and diffraction are both measured and the wave-length found from the general equation—

$$n\lambda = b(\sin i + \sin \theta).$$

This method, of course, has not such a probable accuracy as the first, owing to the fact that two angles have to be measured in place of one; it was, however, used by Ångström in his work. The methods of measurement are as follows, with a transmission grating. When the grating has been put in position, the telescope is turned until the cross-wire is brought upon the direct image and the reading taken; similarly a reading is taken of the reflected image. The angle between these readings subtracted from 180° gives the angle between the incident and reflected rays, and half this latter angle is the angle of incidence. From

these data the reading of the telescope when normal to the grating can readily be found; from this reading to the reading on the diffracted ray gives the angle of diffraction. Care must be taken to note the sign of this angle θ, it being positive when the incident and diffracted rays are on the same side of the normal, and negative when they are upon opposite sides. The values found are then substituted in equation (1), whence the wave-length can be found. Exactly similar procedure holds in the case of the reflecting grating. Equation (2) may also be employed when it becomes necessary to measure the angle of deviation ϕ, that is to say, the angle between (*a*) the diffracted ray and (*b*) the transmitted ray in the case of a transparent grating, and the reflected ray with a metal grating. The angle $i - \theta$ in the case of a transmission grating is obtained as follows: Readings are taken of both the reflected ray and the diffracted ray; the angle between them subtracted from $180°$ is the angle $i - \theta$. In the case of a reflecting grating $i - \theta$ is the angle between the incident and diffracted rays, and may be readily found by reading the direct image before the grating is put in place.

The fourth method, namely, that of minimum deviation, can be used with a transmission grating, and has the advantage of better definition, but is very cumbersome owing to the fact that the grating has to be specially adjusted for each line measured. The condition for minimum deviation, as shown before, is obtained when the angles of incidence and diffraction are equal; in practice the grating is so turned that the angle of deviation becomes equal to the angle between the incident and reflected rays. This method is not often made use of with plane reflecting gratings, owing to the fact that a Littrow type of apparatus is necessary, and as a rule these are made with concave gratings.

The fifth and last method, which was used by Bell in his later determinations of absolute wave-length, consists in working with the telescope and collimator permanently clamped at some known angle with each other. This angle, of course, is the angle $i - \theta$ in equation (2), and, since this is determined once for all, it is only necessary to measure the angle, $i + \theta$ or the deviation. For this purpose it is necessary that the grating be mounted upon a spectrometer table so that its rotation can be measured. In an experiment the grating is so turned that the reflected image of the slit is adjusted upon the cross-wires in the eyepiece of the telescope, when the reading of the rotating grating table is made. The grating table is then turned until the spectrum line required is brought upon the cross-wires, when the reading is again taken. Twice the angle through which the grating has been turned is equal to the angle of deviation. By substituting the value of this angle and the angle between the collimator and telescope in equation (2) the wave-length may be obtained.

A word may perhaps be said here concerning the value of b or the grating space. It will be remembered that this refers to the length of one aperture on the grating plus one adjacent dark space. This may very readily be found from the number of lines which are known to be ruled; Rowland gratings are ruled, except in special cases, with 20,000, 14,438,

or 10,000 lines to the inch, and have therefore grating spaces respectively of 0·00127 mm., 0·001759 mm., or 0·00254 mm., whilst the gratings ruled by the machine at the National Physical Laboratory have 14,400, 7,200, 4,800, or 3,600 lines to the inch, and have grating spaces of 0·0017639 mm., 0·0035278 mm., 0·0052917 mm., or 0·0070556 mm. It will be quite sufficient to take these as perfectly correct for all ordinary work; it is only in cases when very great accuracy is required that the correctness of these numbers comes into question,[1] and under these circumstances, as before pointed out, attention should be turned to other methods of measurement.

It was first shown by Rayleigh that replica gratings can be produced from a ruled grating by simple photographic methods. It is now possible commercially to obtain replicas of Rowland gratings at a very reasonable cost, which are casts in celluloid taken from a good ruled grating. These are generally known under the name of Thorp's gratings, after the discoverer of the process. Thorp's method has been improved by R. J. Wallace,[2] who used gun-cotton in place of celluloid. He dissolved this in amyl acetate, using only the very best quality of gun-cotton, and then poured the solution into water. The precipitated gun-cotton is filtered off and thoroughly dried. The dried cotton is again dissolved in amyl acetate, and the resulting collodion is poured over the grating, care, of course, being taken that all dust is kept away. It is then allowed to dry very slowly, and the film carefully removed from the grating and mounted on a piece of plate-glass, the latter having been previously coated with a film of hard gelatine. It is not easy completely to remove all dust from a grating before taking the collodion cast, and, therefore, it is advisable to reject the first cast made, since this, when detached from the grating, will bring away with it all dust and dirt which was previously adhering to the metal surface. The grating will then be thoroughly clean and any casts now made from it will be free from all defects due to dust, etc. Dr. J. J. Fox has pointed out to me that one of the best possible methods of cleaning a grating is to take a collodion cast from it as described. This is a very useful piece of information as dust and dirt greatly mar the brilliancy of the spectra obtained.

It has recently been found possible to convert these transmission into reflecting replicas by coating them with a very thin metallic film. This is done by Houllevigue's[3] method, and the application of this method to the replica grating is described by Gehrcke and Leithäuser.[4] The metallic deposit is produced by submitting the replica to the kathode rays in a very high vacuum, using a platinum kathode, and the process takes about two hours. The reflecting grating has exactly the same properties as the original.

One of the most convenient mountings for using a plane grating is that known as the Littrow mounting, which is a simple modification of that already described and shown on page 107. This method consists

[1] See page 32 *et seq.*
[2] *Astrophys. Journ.*, **22**, 123 (1905).
[3] *Comptes Rendus*, **135**, 626 (1902).
[4] *Verh. der Deutsch. Phys. Gesell.*, **11**, 310 (1909).

in placing a lens in front of the grating to render the incident light parallel and rotating the grating until the diffracted light is returned along the direction of incidence, and is focussed by the same lens.

The Rowland Mounting of the Concave Grating.—A brief description has already been given of Rowland's method of mounting the concave grating in so far as was necessary to show how the necessary condition was secured of the grating, slit and eyepiece, or camera, always being placed upon the circumference of the same circle, namely, the circle having the radius of curvature of the grating as its diameter. A

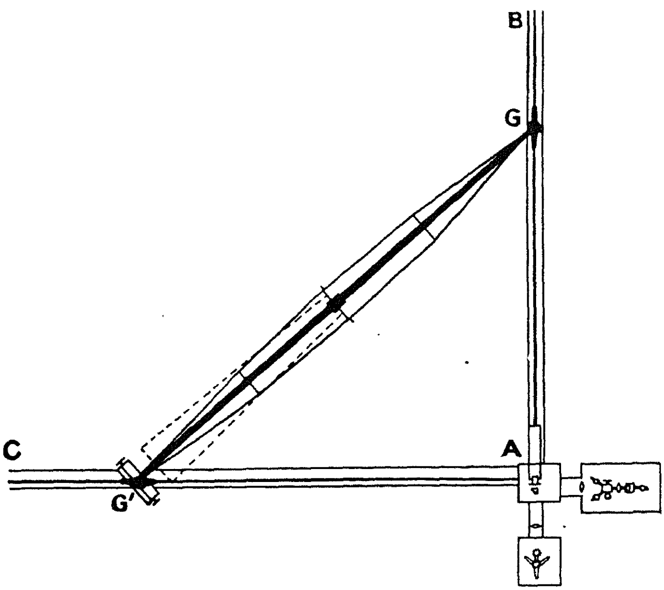


FIG. 85.

description of Rowland's apparatus at the Johns Hopkins University has been given by Ames,[1] from which the following details are taken :—

AB and AC (see Fig. 85) are heavy wooden beams 6 × 13 inches cross-section, and 23 feet long. AB is rigidly fixed, while AC has a slight freedom of rotation about A, controlled by screws at C. The rails for the two carriages carrying the grating, and the camera, are fastened to these beams by screws (see Fig. 86) which admit of adjustment, so that the rails may be straightened if the beams warp. They are made of ½-inch angle iron, although a board made of any hard wood might be used. GG′ is a 4-inch tubular wrought-iron girder braced by a truss, and pivoted at the two ends,

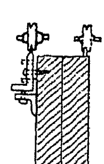


FIG. 86.

[1] *Phil. Mag.* (5), 27, 369 (1889).

directly over the rails, on the two iron carriages. The length of the girder is approximately equal to the radius of curvature of the grating, and there is a range of adjustment of about 6 inches. To the ends of the girder tube are fastened two thick metal plates, and these rest upon the two carriages; these plates are bored to fit over a vertical pin, which is fixed upon the top of each carriage. The carriages each have two brass wheels placed about $1\frac{1}{2}$ feet apart, and these, resting on the rails, enable the girder to be easily moved from one position to another.

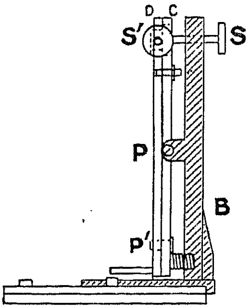


FIG. 87.

One of the carriages carries the grating holder, and the other the camera. The grating holder is shown in Fig. 87; it is made of brass, and consists of a heavy platform, carrying an upright frame, B, which can move in slots on A. Fastened to the two sides of B are two lugs, P, between which the square brass plate C is held by pins, and in this way the plate C can be turned on a horizontal axis. This motion is

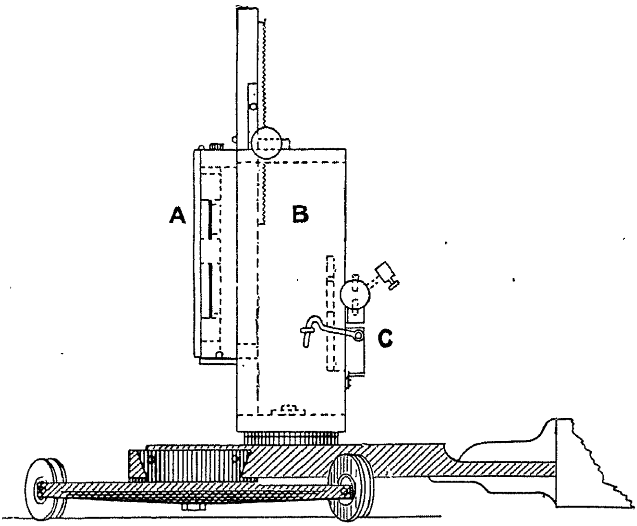


FIG. 88.

governed by the screw S. At the lower end of C is a pin, P′, and on this is fitted a second brass plate, D, which thus can revolve on the axis P′. This motion is controlled by the screw S′, and a spring which is not shown in the diagram. The grating itself stands on two projections from the bottom of D, and is held up against D by soft wax, thus being

free from all manner of constraint. The camera box consists of a fixed wooden frame B, Fig. 88, and a box, A, which can be removed. The photographic plate is placed in A in suitable slots, and is pressed firmly by wooden buttons against pieces of hard rubber, so that it is bent to the proper radius. There is in B a frame which can be moved vertically by a rack and pinion; and to this A is fastened by dowel pins on the bottom and hooks on the top. On the back of the camera box B is hinged a board, C, which can be held firmly in place by hooks. This board carries a brass plate, Fig. 89, having a longitudinal opening of a width equal to the thickness of the plate, and capable of revolution round a horizontal central axis. By means of stops this revolution is confined to 90°. This plate is used for the comparison of spectra.

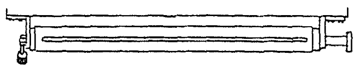


FIG. 89.

The slit used in all grating apparatus must, necessarily, be provided with an arrangement whereby it can be rotated in its own plane, on account of the fact that it is essential for the slit aperture to be truly

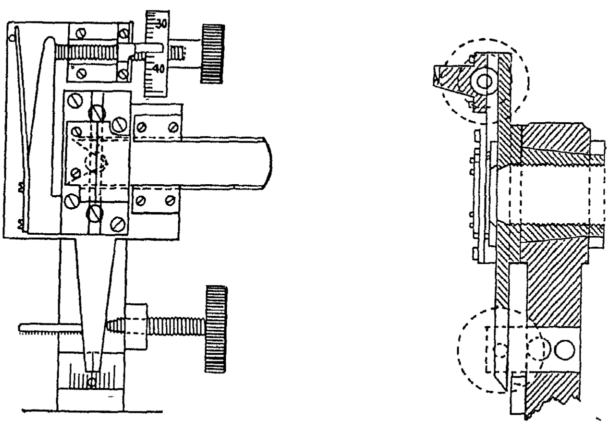


FIG. 90.

vertical and parallel to the rulings on the grating. The slit of Rowland's apparatus is shown in Fig. 90 in front elevation and side sectional elevation; as will be seen from the figures, it can be rotated in its own plane by the lower adjusting screw, while the upper screw is for the regulating of the slit opening. A V-shaped sliding diaphragm is placed over the slit for use with the light of the sun, in order to stop down the solar image, as otherwise the definition may be spoiled by the rotation of the sun.

It is necessary that hoods of black cloth be used to keep out stray light, both at the slit and at the camera box, the latter preferably extending halfway to the grating, for although the apparatus is placed in a

dark room lighted only through ruby glass windows, a certain quantity of stray light is sure to be present.

Kayser, in describing his method of mounting,[1] considers that the fact that the carriages have only two wheels does not ensure their being rigid, that is to say, a small amount of bending of the carriages backwards or forwards is, in his opinion, quite possible with Rowland's arrangement. He therefore uses four-wheeled carriages, two of which run on the rails, while the other pair run on a flat-topped beam fixed parallel to the beam carrying the rails. The wheels are about 2 feet apart, and the weight of the carriages is about 110 lbs. The girder in Kayser's apparatus is a bridge structure, made of hoop-iron, and carries light wooden frames, over which black cloth is stretched.

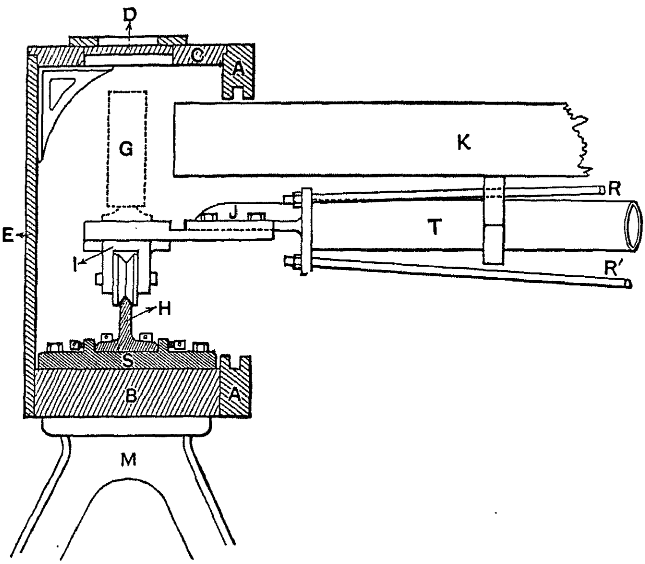


FIG. 91.

It is often necessary, of course, that a grating apparatus be erected in a light room, when it becomes necessary to box the whole apparatus in, and a method of doing this has been devised by Adeney and Carson for the large grating in the Royal University of Ireland.[2] Their arrangement is shown in Figs. 91, 92 and 93, which are taken from their paper. The whole of the grating rail is enclosed on the outer side, and the top as shown at E and D in Fig. 91; AA are two grooved pieces, into which a series of sliding panels can be inserted from either end. K is a wooden rectangular tube, along which the diffracted rays pass to the plate; it is shown in sectional elevation in Fig. 92. As can be seen,

[1] *Handbuch der Spectroscopie*, i. 474.
[2] *Proc. Roy. Soc.*, Dublin (1), **8**, 711 (1898).

the side of this box was grooved for the reception of sliding panels, which extended for about half the length; the necessity for this is clearly shown in Fig. 93, where the dotted line IA represents the side of K, which must be open in order to allow the free passage of the light from the slit to the grating. The amount of opening necessary in the side of K varies, of course, with the position of the camera.

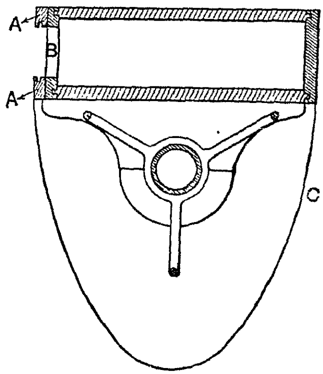


FIG. 92.

The following is a description of the mounting of the 10-foot focus grating at University College, London, which was made in the department, and may perhaps serve as a guide to any one who wishes to make his own mounting.

The whole apparatus is carried on three cast-iron columns, 4 inches n diameter, and 8 feet in height. Each of these columns has a base bout 1 foot square, which is securely bolted down to the concrete floor by four $\frac{3}{4}$-inch bolts, one at each corner, and on the top of each column s rigidly fixed a cap with a flat surface for the support of the beams. The columns are erected at about 10 feet from each other, and so placed s to include as nearly as possible a right angle. Resting on these nd bolted to the caps are two steel girders 5 × 5 inches of I cross-

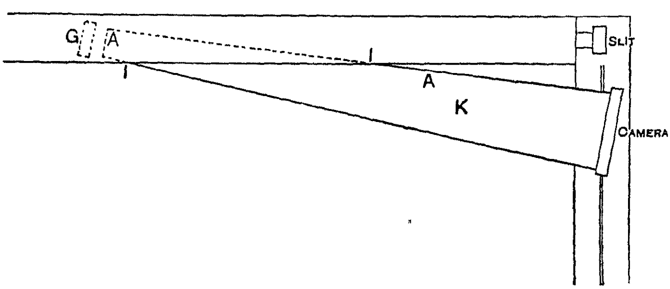


FIG. 93.

ction, and a little over 11 feet long. The girders are thus set as arly as possible at right angles to one another, and both rest on, and bolted to, the cap of the centre column. This forms the main pport of the apparatus. The two rails on which the camera and ting carriages run are of steel 2 × 2 inches of ⊥ cross-section, and feet long. Each rail is supported by fourteen $\frac{3}{8}$-inch levelling ews, which are placed at distances of a foot apart, alternately on each e of the centre web, and two at each end. The lower ends of the

screws are turned to sharp points, which are hardened, and rest on the steel girders. Moreover, each screw is provided with a locknut to clamp it in position when the rail is level. In fitting up the apparatus, when the two rails had been adjusted with sufficient accuracy to a right angle, and properly levelled, each of the screws was smartly hit with a hammer, and thus the sharp-pointed ends punched for themselves small sockets in the girders. After this had been done the rails were again tested with a level and again adjusted.

In this way, since the points of the screws rest in the sockets, no lateral shifting of the rails is possible unless they are lifted in any way, and this is obviated by firmly fixing them down by two angle pieces at

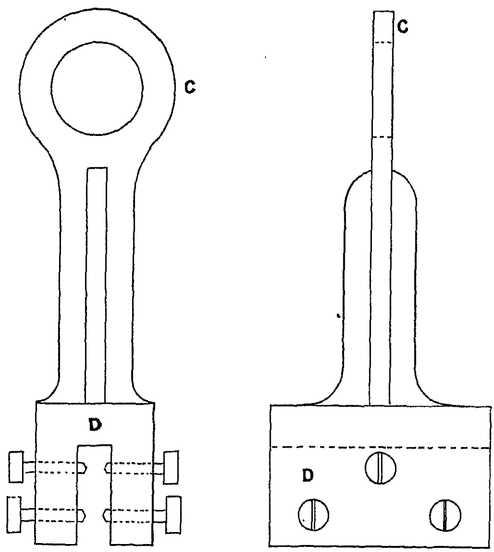


FIG. 94.

each end of the two rails, which are held by screws into the steel girders. The centre webs of the rails were planed, which gives a sufficiently level surface for the carriages to run upon. By this method of mounting, certain conveniences are obtained, notably in the lightness of the rails themselves. This lightness has no disadvantage, for, supported as they are at such close intervals by the levelling screws, there can be no possibility of any sinking of the rails in any way under the weight of the carriages.

The slit is mounted on a special casting shown in Fig. 94 in side and front elevation. The slit itself is mounted upon a tube which slides into a flanged tube, and this flanged tube is screwed to the annular plate C. This plate C is about 3 inches outside diameter, and about $\frac{5}{16}$-inch thick. The upright standard which supports C is of + cross-

section, as is shown in the diagrams. The bottom block D, which is about 4 inches long, is slotted in order to admit the centre web of the grating rail. The plate C was faced up in a lathe, and the slot in the base was planed out so as to be true and square to it, this being, of course, necessary in order to bring the slit into correct alignment with the grating, when the base is fitted over the grating rail. As can be seen from the diagram, three screws are set in each side of the base, which serve to clamp the apparatus in position on the rail, and by their means the position of the slit can be adjusted with great accuracy.

The two carriages which carry the grating and camera are identical

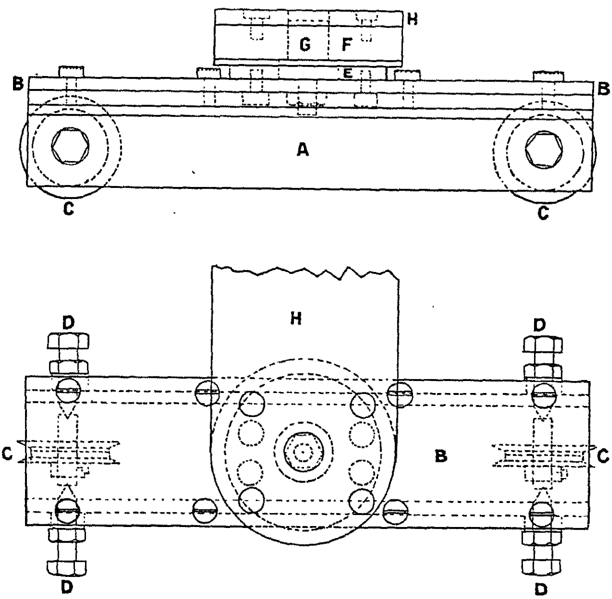


FIG. 95.

in construction, and are shown in Fig. 95, in plan and side and end elevation. AA are two iron castings, 12 inches long, 2 inches wide, and $\frac{1}{4}$ inch thick; they widen, as shown, at the top, in order to offer more substance to the screws. These castings are planed on their top edges, and they form the sides of the carriages. The top B is a planished brass-plate, 12 × 3 inches, and $\frac{1}{4}$ inch thick, and this is screwed down on to the planed top edges of the side pieces by four screws on each side. The two wheels CC are gun-metal, and are about 2 inches in diameter, and are mounted on $\frac{3}{8}$-inch steel axles. These wheels are supported by the $\frac{3}{8}$-inch set-screws DD, which pass through bosses on the cast-iron side pieces. These set-screws are pointed, and the ends of the axles of the wheels are drilled to receive them; the screws also carry

locknuts to clamp them in position. The distance between the centre of the wheels is about 10 inches, the side pieces extending about 1 inch at each end beyond the set-screws. The large vertical bearing, by means of which the beam connecting the two carriages is supported in each case, consists of two gun-metal discs, 4 inches in diameter, which work against one another round a centre steel pin. The construction of the joint is shown on the carriage at EFG. E and F are the two gun-metal discs, the lower one, E, being $\frac{3}{8}$ inch thick, and the upper one, F, $\frac{3}{4}$ inch thick. The centre steel pin is shown at G, and is $\frac{7}{8}$ inch in diameter where it passes through F, and $1\frac{1}{4}$ inch where it passes through the disc E. Below E it is turned down to $\frac{3}{8}$ inch, and, passing through the brass top of the carriage B, it is screwed and nutted underneath. Both of the discs are accurately turned and bored out to fit the steel pin, and to work with the greatest possible smoothness against one another. The lower disc E is fastened by four screws on to the carriage top, as is shown in the plan, whilst the upper disc F, as shown at A, Fig. 96, is fastened to a plate forming part of the beam connecting the two carriages. Fig. 96 is a diagram, drawn to quarter of the scale of Fig. 95, of the construction of this beam, and shows half of the beam in elevation and in plan. As mentioned above, the upper disc of the carriage bearing is shown at A; the disc is fastened by screws to the plate H, which is of mild steel, 14 × 4 inches, and $\frac{3}{8}$ inch thick, and is planed on both sides. As shown in the plan, this plate H is rounded off at the end over the disc in order to make the appearance as neat as possible. A $\frac{7}{8}$-inch hole was drilled in the mild steel plate, as shown, to admit the top of the steel pin of the bearing, which projects through the top disc, as shown at G, Fig. 95. This was arranged simply as a matter of convenience in fitting the apparatus together. The beam itself, as shown in Fig. 96, is very simple in construction, and was designed to be as light and, at the same time, as rigid as possible. It is made of bicycle tubing, stayed with three steel wires. This tube, which is marked C in the figure, is 7 feet 2 inches long, and 1 inch in diameter, and about $\frac{3}{64}$ inch thick in the walls. At each end this tube is brazed on to a lug, D, which projects about 2 inches from a cast-iron plate, E, which is 4 inches wide—the same as the mild steel plate—about 1 foot long, and $\frac{1}{2}$ inch thick. These cast-iron plates were planed on the under sides, and the lugs carefully turned in a lathe so as to be true to the planed surfaces, and just to fit the bicycle tubing. The brazing of the two ends of the tubing on to the lugs was one of the most difficult operations of the whole mounting, for it was absolutely essential to obtain the planed surfaces of the cast-iron plates at each end of the beam perfectly true to one another. The whole success of the mounting depended on this, and care was especially taken to guard against any twist. This operation was successfully carried out, and the two planed surfaces are almost absolutely true to one another.

The three staying wires are made of the best stout piano wire, and are carried from brackets on the cast-iron plates at each end over a three-winged support in the middle of the tubing. As can be seen in the dia-

gram, two of the brackets are on the top of the cast-iron plates, and one underneath. Their design is quite simple, and sufficiently indicated

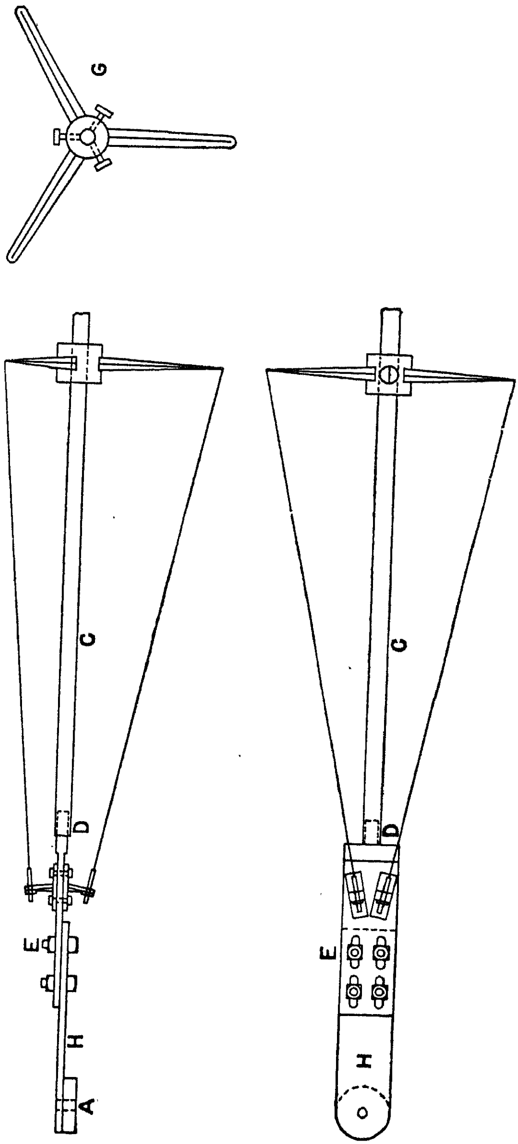


FIG. 96.

the figure. They are of gun-metal, and are fastened by a screw at ch end into the cast-iron plates. The three stay wires at each end are

brazed into $\frac{1}{4}$-inch bolts, which are about 4 inches long, and screwed the whole length. These bolts pass through holes drilled in the brackets, and are nutted at the back. There is thus 4 inches of adjustment at each end of the wires to take up stretching. The three-winged support for the wires in the middle of the beam is a gun-metal casting, and is shown at G, Fig. 96. Each wing is 10 inches long, and the whole is so placed that one wing points vertically downwards, whilst the other two enclose rather a wider angle than symmetry requires—it is about 130°. This was done in order to prevent any interference with the spectrum as it passes between them. The centre block of the casting was bored out so as to fit the bicycle tube, and three set-screws symmetrically placed serve to hold it in position. The three wires are very tightly stretched, care being taken that no distortion is caused to the beam by reason of any unequal tension in the wires. As regards the joining of the beam to the mild steel plates, this is done in each case by 4 $\frac{1}{2}$-inch bolts.

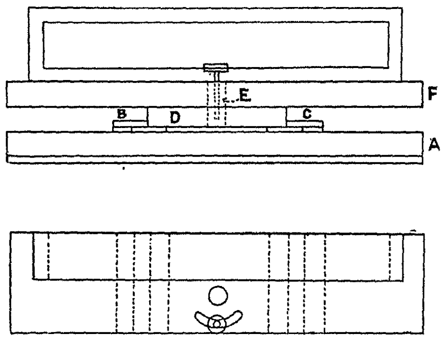


FIG. 97.

Both the cast-iron and the mild steel plates at each end of the beam are slotted, to allow of some latitude in the length of the beam, which may be required when the final adjustments are being made.

The supports carrying the camera in one case and the grating mounting in the other case are of necessity somewhat different. At the camera end of the beam, a planished brass plate, 18 inches long, $4\frac{1}{2}$ inches wide, and $\frac{1}{4}$ inch thick, is screwed to the mild steel plate exactly at right-angles to the beam, and so placed that its centre is exactly over the centre of the steel centre pin of the bearing. This brass plate carries a mahogany board of the same area, but 1 inch thick. This is shown at A, Fig. 97, and in this diagram are drawn the complete camera fittings, the most important of these being the adjustments for focussing. The adjustment normal to the grating is obtained by the use of the brass slides, shown at B and C. These are $4\frac{1}{2}$ inches long, and are made of $\frac{3}{16}$-inch brass. Each bearing consists of brass strips, B and C, $1\frac{1}{2}$ inch wide, which are screwed to the mahogany board, but are separated from it by distance pieces of half their breadth. The strips therefore project about $\frac{3}{4}$ inch

over the distance pieces, and thus form a groove into which the corresponding brass fittings on the upper board D exactly fit. A rotary adjustment is also possible between small limits, and is obtained as follows:—

In the centre of D is erected a $\frac{1}{2}$-inch brass pin, E, which fits into a brass tube carried by the upper board F. This allows a rotary motion to be given to F, the amount of which is controlled by a set-screw into the lower board D, passing through the slot shown in the plan. The board F forms the support of the dark slide. A mahogany frame, G, is fastened by screws on to the top of F, and has a clear opening of 14 × 4 inches, and is 2 inches deep. The dark slide is tightly held up against this frame by two brass hooks at the sides, and good contact between the two is ensured by strips of velvet glued to the back edges of the frame. The dark slide requires no special description. It is made to carry plates 12 × 2 inches, which are specially made of thin glass, and are bent to the required curve, namely, a circle of 5 feet radius. This is accomplished in the usual way, by fixing two carefully cut templates in the slide, and pressing the plate against these by rubber pads on the back of the dark slide. It should be said, of course, that the back is detachable, and that when a plate has been put in, the back is fastened down by catches, and forces the plate round the templates.

As regards the mounting of the grating on its carriage, a $\frac{3}{16}$-inch planished brass circular plate, 8 inches in diameter, is screwed down to the mild steel plate (H, Figs. 95 and 96), centrally over the bearing on the carriage, and on to this plate is screwed the bottom plate of the grating mounting. This is a plate about $5\frac{1}{2}$ inches in diameter, and has three radial slots cut in it, in which the three levelling screws of the grating table rest.

This completes the description of the actual mounting of the grating apparatus, and it only remains to describe the covering in of the apparatus, the method of which is as follows. Two boards, 18 × 6 inches, and 1 inch thick, are fastened, one across the top and the other across the bottom of the cast-iron and mild steel plates at E, Fig. 96, at the camera end of the beam. Both these boards are recessed to admit the bolts and plates just sufficiently to allow them to meet, and they are screwed firmly together.

These two boards serve as a support for two iron brackets, which are screwed to the top board. Two similar brackets are also erected just behind the grating, on the 8-inch circular brass disc mentioned above. Four thin iron strips about 1 inch wide are stretched along the beam, two between each outside pair of brackets, and are kept in tension by bolts and nuts. The bolts are brass, and are soldered to the iron strips, and pass through holes in the brackets. These four bands, one at the top and bottom of each bracket, form a support for two thicknesses of sateen, which are stretched tight and stitched all along each strip.

In order to keep the iron bands in their position, that is to say, to keep them from closing together when the sateen is stretched over them, distance pieces are placed at suitable intervals between the upper pair

and the lower pair of bands. These distance pieces are quite light, being only of wood 1 inch square, and are held in their positions by screws through holes drilled in the iron strips.

The two brackets at the camera end are placed about 3 inches in front of the frame against which the dark slide is placed, and the space between is covered by sateen, which is quite loosely stretched between the brackets and the frame, to allow of a certain amount of adjustment in the position of the dark slide for purposes of focussing.

In order to admit the passage of the light from the slit to the grating, the sateen between the two iron strips opposite the slit is cut away, just as far as is necessary to admit the light from the slit when the camera is brought near to the slit. It follows, therefore, that when the camera is moved to the other end of its rail, the grating becomes exposed to the ordinary light of the room through this opening. The exposed portion is covered over with a dark cloth, this being found quite sufficient to make it light-tight.

Seeing that the four iron strips have to be kept in considerable tension, in order to hold them moderately rigid, a certain amount of displacement will be caused to the beam by this means. An extra stay of steel wire was put underneath the beam, between two brackets, similar to those already described; this was found to counteract the strain set up by the iron strips.

For the covering in of the grating rail, a simple method has been adopted. A wooden framework was erected over the girder, which carries the rail. This framework is made of 2-inch square mahogany, and is about 1 foot wide, and 20 inches high. The top, the outer side, and the two ends, are covered with light wooden boards, about $\frac{1}{4}$ inch thick. The front side, that is to say, the side along which the beam has to pass, is filled in with two curtains, running on wires. Two wires are tightly stretched between the supports at each end of the frame, one at the top and one at the bottom. Two curtains—each capable of stretching along the whole frame, that is to say, about 11 feet—are threaded on these two wires. One end of each of these curtains is nailed to the frame support, one at each end of the girder, and one curtain is put on each side of the beam. It is evident from this that whatever the position of the beam may be, these curtains may be drawn right up to each side of it. This shuts out practically all light. Although the two wires which carry the curtains are placed as close as possible to the top and bottom of the frame, still a certain amount of light will necessarily be able to pass above and below them. As regards the top, this is easily obviated by a short curtain, which is nailed all along the top of the frame, and which, by simply hanging down, keeps all the light out. As regards the bottom, it might be arranged to have a short fringe stretched along the two curtains, which would answer the purpose, but it has been found more convenient to use ropes of twisted black cotton-wool, which are placed along the frame under the curtain. It would be possible, no doubt, to have a light metal frame to run on the curtain wires, through which the beam could pass. If the two

rtains were fastened to the two sides of this, the adjustment of the rtains would become automatic. This, however, has not been opted, because it is such an easy matter moving the curtains by hand er the camera-carriage has been set in the right position.

Wadsworth[1] has devised several methods of mounting concave ıtings, which partake of the fixed-arm type. These are, perhaps, ɔre especially intended to adapt the instrument to astronomical purses. One of these, however, may be described here, although it does ıt strictly belong to the fixed-arm type. This arrangement is shown Fig. 98, and, as will be seen, the principle is the same as in Rowıd's mounting; it differs from this, however, in that the diffracted ys from the grating G do not travel direct to the eyepiece, but are flected by a plane mirror, C, to the eyepiece or plate at O. The ating is mounted upon a sleeve which slides over the rod GS, and the o ties CG and CS are linked together at C, and pivoted at G and S spectively. The slit is fixed at S, and the spectra are made to pass in ɔnt of the field of view in the eyepiece, by sliding the grating sleeve ɔng its rod.

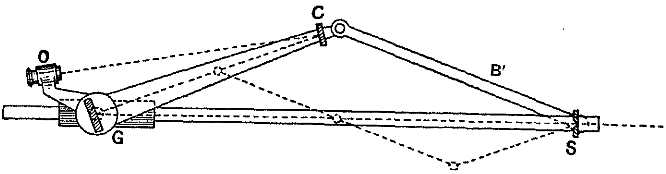


FIG. 98.

Wadsworth[2] has also devised a special mounting to utilise the stigmatism of the grating, as pointed out by Sirks, which is as follows. et G, Fig. 99, be the position of the grating, s the slit, r the source or ıe reflecting prism, and O the observing eyepiece, placed normal to ıe grating, and at a fixed distance ρ from it, as in Rowland's mounting. 'hen the slit must lie always on the circle $Os''ss'$ of radius $\frac{\rho}{2}$, whilst the ɔurce r lies at the intersection of Gs produced and the line Or, drawn t right angles to GO.

'hen $$Gs = 2GQ\cos i = \rho\cos i$$

nd $$Gr = \frac{\rho}{\cos i}, \text{ or } sr = Gr - Gs = \frac{\rho}{\cos i} - \rho\cos i.$$

To satisfy these conditions it is necessary to mount the slit on the nd of an arm of length $\frac{\rho}{2}$, pivoted at Q, and also we must have from he geometry of the circle $Gs \times Gr = (GO)^2 = \rho^2 =$ constant.

This can be obtained by means of the Peaucellier linkage shown in

[1] *Astrophys. Journ.*, **2**, 370 (1895). [2] *Ibid.*, **3**, 46 (1896).

13 *

Fig. 99; in it we have $ae \times ac = ab^2 - be^2$, which, to satisfy the abov condition, must equal ρ^2.

Hence, if we place the source or comparison prism at C, and pivc the vertices e and a to the ends s and G of the links Qs and QG re

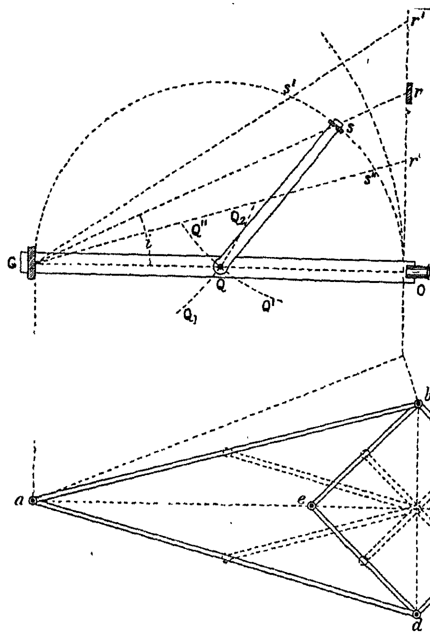


FIG. 99.

spectively, the desired conditions will be obtained, and we will have the simple mountings shown in Fig. 100. We may either fix the pivot at G, the pivot at s, or the pivot at r in position. If G is fixed, Q may

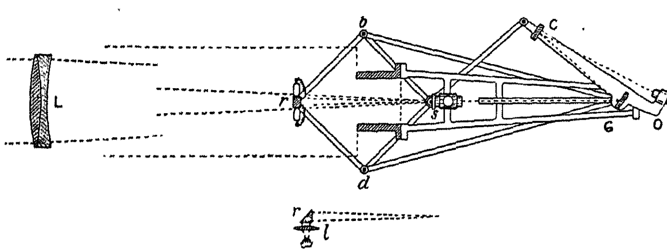


FIG. 100.

also be fixed, in which case O also remains fixed; but the slit and comparison prism r slide along the line Gsr, while this line itself rotates about the pivot G. A simpler arrangement, therefore, is obtained by

fixing either the pivot *s* or the pivot *r*, leaving Q free. Then the grating and comparison prism, or the grating and slit, slide along the bar G*sr*, which remains fixed, and the point Q describes a curve Q′QQ″ (if *s* is fixed) or Q_1QQ_2 (if *r* is fixed), the centres of which at any instant are at G and *s*. The eyepiece O will, therefore, describe a similar curve of twice the radius about G as a centre, and, in order to avoid this large range of motion, as well as the long arm GO, we may place a reflecting plane mirror at C (Fig. 100), and return the rays to an eyepiece O near G. In Fig. 100 the slit is fixed at *s*, so that the comparison prism at *r* and the grating move; in the diagram a vacuum tube is shown at *r* as a comparison source.

The Adjustment of the Concave Grating (Rowland Mounting).—Ames [1] gives the following directions for the adjustments of the various parts of the apparatus. First, the two beams are made as level as possible, and placed at right angles by the 3, 4, 5 rule. Distances from the intersection of the rails proportional to 3 and 4 are accurately marked out on the two beams respectively, and the beams adjusted until the distance between the two points thus found is proportional to 5. Next, the axes at the ends of the girder must be made parallel, while the girder is under stress; for this purpose the girder is supported at its two ends, and the axis adjusted by the control screws until the axes are vertical. The camera, grating, and slit are now put into position at the proper height, care being taken that the grating is so placed that the brightest spectra are observed, for, as was pointed out before, the spectra obtained with a grating are generally brighter on one side than on the other. A candle is held at the centre of the camera-box, immediately over the axis of the carriage, and the grating is turned, and the girder lengthened, until the flame and its image coincide. In this way the grating is placed perpendicularly to the girder, and the girder itself is given the proper length. To adjust the camera so that it is perpendicular to the girder, a piece of plate glass is fastened to its face, and a candle is held on the girder near the grating. The camera is then turned until the flame and its image come into line. Light from some source is now thrown on to the slit so as to illuminate the whole grating, and the spectrum is observed at the camera, and, if necessary, the grating is tilted more or less until the spectrum is seen in the middle of the camera. The girder is then moved about, and if the spectrum thereby tends to rise or fall, the grating is revolved in its own plane by the side screw of its holder (S′, Fig. 87) until this is corrected. Finally, the slit is revolved until the best definition is secured. The instrument should now be in perfect adjustment, which may be tested as follows: an exposed and developed photographic plate, of which the emulsion has been partly scraped off so as to give it a lattice-work appearance, is put in the camera-box, emulsion side towards the grating. The spectrum is then observed with an eyepiece, and at any position of the girder the emulsion on the plate and the spectrum ought always to be

[1] *Phil. Mag.* [5], 27, 369 (1889).

in the same focus. Generally, however, this will not be the case, and from the theory of errors developed in the earlier part of his paper, Ames recommends a slight adjustment of the grating around its vertical axis, for this generally corrects the above defect.

Kayser[1] gives a rather more detailed account of the methods of adjustment which he has himself employed, and which may be quoted here.

In the first place, he considers Ames's 3, 4, 5 rule to be insufficiently accurate, and recommends the use of a theodolite placed exactly over the intersection of the rails; he then adjusts the beams until the angle measured between them is exactly equal to 90°. For the adjustment of the grating and camera over the axes of their carriages, small pointed metal pins are fitted exactly in the centre of the axes, holes having been bored in the centres when the axes were first made. By means of a plumb-line the surface of the grating and the emulsion of a plate in the camera are brought over these points. Kayser also gives a more accurate method for the adjustment of the length of the girder and the position of the grating. An exposed and developed plate is taken, and about 1 cm. from the middle a cross is cut in the emulsion, and exactly the same distance on the other side of the centre a portion of the emulsion is scraped off, and some scratches made on the glass, with a diamond. The plate is then put in position in the camera, and a small totally reflecting prism is fastened with soft wax to the outside of the plate behind the cross. A beam of light from a side source is thrown through the cross on to the grating, and, if the adjustments are correct, the image of the cross should be focussed on the clear glass, and thus the scratches and the image of the cross should be seen together in perfect focus through an eyepiece. The grating must be turned and the length of the girder altered until this condition is secured.

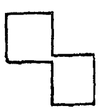


FIG. 101.

A convenient method for the testing of the adjustments is to cover the grating with a diaphragm shaped as in Fig. 101, which leaves two opposite quarters exposed. Clearly these portions of the grating will give a continuous line if the adjustments be correct, and two slightly displaced lines if they be not correct; in the latter case, from the positions of these displaced lines, the amount of error in the focus may be calculated.

Practical Use of the Concave Grating (Rowland Mounting).—Although the use of the Rowland mounting of the concave grating for the determination of wave-lengths by the method of coincidences has been found to be untrustworthy, the following account of the practical use of the concave grating may be given for two reasons. In the first place, it will enable Rowland's method of work to be understood, and in the second place it may prove of assistance to those who wish to use his method of mounting a concave grating for the de-

[1] *Handbuch der Spectroscopie*, i., 475.

termination of wave-lengths by the now accepted method of interpolation between international standards, this method being, of course, independent of the type of mounting used.

From what has already been stated under the theory of the grating in the last chapter, it is necessary that the grating be carefully examined with respect to the distribution of the light in the various orders; for it is quite possible for the grating to give an incomplete spectrum in a given order; for example, the visible portion may be very bright and the ultra-violet very weak. Further, as pointed out by Ames, different portions of the grating may give spectra of varying brightness, and these imperfections must be guarded against for accurate work.

As regards choice of grating, it is only when work is to be done with the camera in the ultra-violet that it becomes necessary to use a 20,000 line grating, and as, further, a 10,000 line instrument has the advantage in point of definition and cheapness, therefore, for ordinary work the latter or a 14,438 line instrument should be chosen. The practical ranges of the various-sized gratings were given before on p. 164, but they may be given more fully here. Fig. 102 is a diagram of the overlapping spectra as obtained with the various instruments. The extent of the first five spectra reached is given in the table at top of following page.

These limits are taken at the centre of the photographic plate. At the end of the plate, of course, the limit is somewhat greater. With a grating of 21·5 feet radius, the width of the spectrum varies from $\frac{1}{4}$ inch to 4 inches.[1]

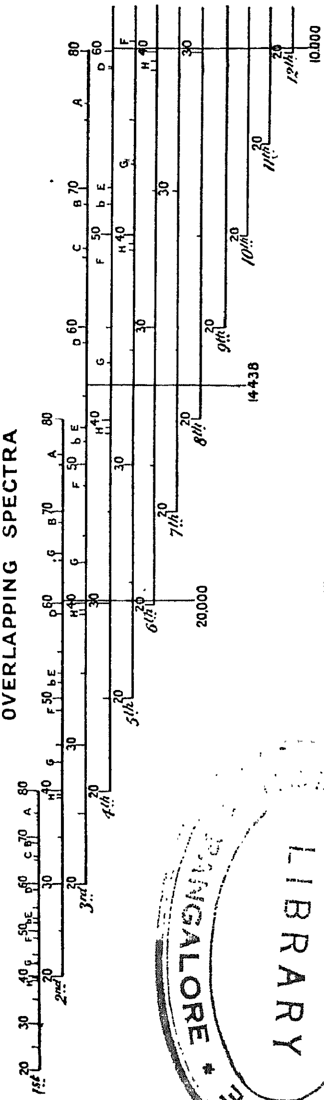


FIG. 102.

[1] See p. 165.

Lines per inch.	First spectrum.	Second spectrum.	Third spectrum.	Fourth spectrum.	Fifth spectrum.
10,000	Entire	Entire	Entire	To 6000	To 4800
14,438	Entire	Entire	To 5760	,, 4330	,, 3460
20,000	Entire	To 6000	,, 4000	,, 3000	,, 2400

The scales may readily be calculated from the formulæ on p. 164, and for the largest size grating of 650 cm. focus they are given by Ames as follows:—

Lines per inch.	First order.	Second order.	Third order.	Fourth order.
10,000	0·26	0·51	0·77	1·03
14,438	0·37	0·75	1·12	1·50
20,000	0·52	1·03	1·55	2·07

The numbers given for the various orders represent the linear distance in millimetres on the photographic plate, corresponding to a change of wave-length of one Ångström—this being, of course, at the centre of curvature of the grating. For gratings of shorter radii these numbers are simply to be multiplied by the ratio of the radii.

When in observing a particular spectrum it is required to cut off the overlapping spectra, certain absorbing media may be used, these being placed, of course, between the slit and the light source. The following are recommended by Ames, and the regions of spectra given are those transmitted by the absorbents:—

Greenish plate glass	3300–8000
Saturated solution of salicylic acid in alcohol in quartz cell	3500–8000
Aesculin, 0·25 per cent. aqueous solution with one drop of ammonia to each 30 cc.	4100–8000

This must be freshly prepared, as it rapidly oxidises to a brown colour.

Potassium ferrocyanide	4400–8000
Primrose or aniline yellow	5000–8000
Fluorescein or gold chloride	5200–8000
Chrome alum . . Malachite green . Bitter almond green Brilliant green . . }	3200–3700 and 4600–5200
Cobalt chloride	3400–4500
Gentian violet, strong	3600–4600 and 6000–8000
Potassium permanganate	3900–4600 and 5800–8000

An an example, when photographing in the fourth order with a 10,000 line grating, the following absorbing solutions are used:—

At 3800 Cobalt chloride in water.
,, 4000 Cobalt chloride or Gentian violet in water in a glass cell.
,, 4200 Potassium permanganate or Gentian violet in water.
,, 4400 Aesculin or Potassium permanganate.
,, 4600 Aesculin.
,, 4800 Aesculin and Malachite green in water.
,, 5000 Aesculin and Potassium ferrocyanide.
,, 5200 Aesculin and Potassium ferrocyanide.
,, 5400 Aesculin and Primrose.

It is advisable that before the use of any absorbent an experimental photograph should be taken in order to observe its effect.

For regions beyond the C line and into the infra-red, special absorbents are required, and amongst others the following may be mentioned as having been used by Abney—a solution of potassium bichromate, or a solution of iodine in carbon bisulphide.

Wood[1] has discovered that nitrosodimethylaniline, when in thin layers, has an absorption band between the limits $\lambda = 5000$ and $\lambda = 3900$, but beyond the latter it is transparent to as far as $\lambda = 2000$. This substance may be used, therefore, in order to photograph the ultra-violet spectra free from overlapping higher orders. For this purpose a gelatine film, stained with the nitroso body, is fairly suitable, but a better way is to make a solution in glycerine, and use it in a quartz cell; as the glycerine is acted upon by ultra-violet light, Wood recommends the use of a small quartz cell, made by cementing two quartz plates together with a space between of 0·5 mm. This cell should be cemented to the bottom of a thistle funnel with a very small bore. By filling the thistle funnel with the glycerine solution, a flow takes place through the cell at the rate of about a drop every two minutes. The exposure must be much increased when using the screen, and varies from two to twenty times the ordinary, according to the density of the screen. In the case of weak spectra, the increased time of exposure rather precludes the use of this substance, and under these circumstances it is necessary to take comparison photographs for the purpose of recognising the ultra-violet lines. Two photographs are taken—one of the complete overlapping spectra, and the other with the ultra-violet portion cut off by means of suitable absorbents; the lines present in the first photograph and absent in the second are the ultra-violet lines.

On account of the astigmatism of the concave grating, the usual method of comparing spectra by throwing the images of the two sources adjacent to one another on the slit is not possible, as the two spectra will overlap so considerably. Rowland's method is to employ the mechanical device described on p. 185, which consists of a metal plate with a horizontal slot cut in it exactly equal to the width of the plate (Fig. 89). When in use this plate is turned to a vertical position, and

[1] *Phil. Mag.* (6), 5, 257 (1903).

a photograph taken of the spectrum from some source through t slot; the plate is then turned through 90° to a horizontal position, a the comparison spectrum photographed. When the plate is develope it will be found to have the comparison spectrum with a narrow ba of the first spectrum along its centre. In case of any possible mov ment of the camera during the process, the first spectrum is usua given half the correct exposure, then the second is taken, and finally tl first again to complete its exposure; in this way any chance moveme of the camera will be detected.[1]

Rowland's Coincidence Method of Measurement of Wav length by Means of the Concave Grating.—As has already bee explained, Rowland employed the concave grating for the determinatic of wave-lengths in relation to a chosen standard by the method coincidences, which is based upon the simple relation between the ove lapping orders and the normality of the spectra observed.

The standard adopted by Rowland was the value for the D_1 lir taken by him as a weighted mean of Bell's and other measurements.

In the following table are given the values of the coincidence between this line and points in different orders. The table reads dowr wards—that is to say, the vertical columns give the coincidences :—

Order 1	5896·156			
,, 2	2948·078	5896·156		
,, 3	1965·385	3930·771	5896·156	
,, 4		2948·078	4422·117	5896·156
,, 5		2358·462	3537·694	4716·925
,, 6		1965·385	2948·078	3930·771
,, 7			2526·924	3369·232
,, 8			2211·059	2948·078
,, 9			1965·385	2620·514
,, 10				2358·462

The table, therefore, shows that on the D_1 line in the first order ar superposed 2948·078 in the second order, and 1965·385 in the third and again on D_1 in the third order are superposed 4422·117 in the fourth, 3537·694 in the fifth, and so on.

The method of working is as follows: photographs are taken of the D_1 line in as many orders as the grating allows; in the case of the 20,000 line grating, this can only be done in the first two orders, but with a 10,000 grating, D_1 can be photographed in the first four orders. Care is taken that the D_1 line is approximately in the centre of the plate. On each side of the D_1 line on the photographs will be found a number of lines in different orders, and if the orders to which these lines belong be found by the use of absorbents, then their wave-lengths may be approximately obtained by measuring their distance from the D_1 line on the plate, and by calculation from the scale of the instrument. Ames's values of these scales were given above; it must, of course, be

[1] *Vide* p. 212.

remembered that these can only be quite approximate, and that therefore the wave-lengths we have obtained from our measurements can only be correct to a first approximation.

After this has been done these new lines are again all photographed in different orders from before, in such a way that two, at least, of them are obtained on every plate within the range of normality. The distance between them is measured on the new plates, and from the approximate wave-lengths found in the first place more accurate values are obtained of the scale of the instrument. This more accurate scale value is used for a recalculation of the wave-lengths of the chosen lines on the first plates to a second and closer approximation. With these new values the scale of the instrument is again calculated from the second set of plates, and so on until the limit of accuracy is reached. This limit is of the order of 0·003 A., with the best apparatus, and this Kayser considered to be the mean error of his wave-lengths of the principal lines in the arc spectrum of iron determined by this method.

An accurate value of the scale of the instrument may be obtained by measuring the whole distance from D_1 in the first order to D_1 in the second order. For this purpose a complete series of photographs are taken of the normal spectrum from end to end, and the linear distance between these two lines measured, working from plate to plate. The change in wave-length between the two lines is, of course, 5896·156 A. in the first order, and from this the scale may be obtained. Lines between the two may be measured, and their wave-lengths found, from which the scale may be checked from plates containing more than one of these lines, as described above.

Rowland,[1] in his work on the solar spectrum, determined—

1. The wave-lengths of fourteen lines in the visible spectrum by measurements with a travelling micrometer eyepiece, and these were used as primary standards.

2. The solar standards were measured from one end of the spectrum to the other many times, and a curve of error drawn to correct these primary standards.

3. Flat gratings were also used.

4. Measurements of photographs were made which had upon them two portions of the solar spectrum of different orders. The blue, violet, and ultra-violet spectra were compared with the visible portion, giving many checks on the first series of standards.

5. Measurements were made on photographic plates having the solar spectrum in coincidence with metallic spectra; often of three orders giving the relative wave-lengths of three parts of the spectrum.

Often the same line in the ultra-violet had its wave-length determined by two different routes back to two different lines in the visible spectrum. The agreement of these in nearly every case to 0·01 A. showed the accuracy of the work.

6. Finally, the important lines had from ten to twenty measurements

[1] *Phil. Mag.* (5), 36, 49 (1893).

on them connecting them with their neighbours, and many points in the spectrum both visible and invisible; and the mean values bound the whole system together so intimately that no changes could be made in any part without changing the whole.

Rowland expresses the accuracy of his map as follows: distribute less than 0·01 A. properly throughout the table as a correction, and it will become perfect within the limits 2400 and 7000 A.

Roland's wave-lengths are given, as measured in air, at 20° C. and 760 mm. pressure. As regards the influence of change of atmospheric conditions on the accuracy of the above method, it can readily be shown from the values for the refractive indices of air given on page 41 that, within the limits of 15° to 25° C. and 740-780 mm. pressure, the errors produced lie within the greatest experimental accuracy, and may therefore be neglected.

As was stated previously (pp. 34 and 198) the method of coincidences between the different orders has been proved by Kayser to be quite unreliable and as a result of this the method has entirely been abandoned for accurate work. When Michelson published his first values of the wave-lengths of the three cadmium lines, the differences between these and Rowland's values shook the confidence that had been placed in the latter's work. The actual values were

Michelson	6438·472	5085·824	4799·911
Rowland	6438·680	5086·001	4800·097
Difference	0·208	0·177	0·186

The differences are not proportional to the wave-lengths, and though Rowland felt that a better value for the D_1 line might be obtained, he was convinced that all his measurements were relatively correct to within 0·005 A. Kayser had been for some time assured from an extensive use of Rowland's tables that the system was less accurate than had generally been supposed, and in his measurements of the spectrum of iron he had attempted to amend it,[1] but these measurements had the same general features as Rowland's standards.

There are two reasons for the bad results. As is well known, Roland used the solar spectrum as his standard and he did not know of the difference between the position of arc and solar lines, a difference due to variable pressure effects in the sun. Even the first step of taking the solar D lines for the arc spectra was doubtful. According to Jewell,[2] as Rowland was not convinced that the displacement was due to any other cause than the accidental movement of the apparatus, when changing from the spectrum of the sun to that of the arc, the displacement was treated as being due to this cause, and the wave-lengths of all metallic lines corrected for the average displacement of the stronger "impurity lines" (generally iron) upon the plate, thus reducing them to an approximate agreement with the corresponding solar lines. Kayser[3]

[1] *Ann. der Phys.*, 3, 195 (1900). [2] *Astrophys. Journ.*, 3, 89 (1896).
[3] *Ibid.*, 19, 157 (1904).

pointed out that Rowland thus shifted different parts of the spectrum to smaller or greater wave-lengths, and as from such parts by the method of coincidences other parts were determined, perhaps with another shifting, it is impossible to know to what extent the errors may have accumulated in different parts. If this were the only error, it would be possible to avoid it by applying the method of coincidences, using only the arc lines as determined by Fabry and Perot.

There is, however, another cause for the inaccuracy of Rowland's measurements. As it is impossible to get absolute measurements with the grating, the method of coincidences has also been found to lead to errors. Indeed, Michelson showed that an error in the ruling of gratings is possible, which falsifies the results of this method, and there may be other causes not yet found with the same effect. Kayser carried out some tests of the method with the help of two of Rowland's largest gratings, which were ruled on different engines. With the first grating plates were taken containing Fabry and Perot's lines at $\lambda = 5302$ and 5434 in the second order, coinciding with $\lambda = 3550$ and 3630 in the third order. The wave-lengths of the third order lines were determined from Fabry and Perot's values. Then other plates were taken of these lines in the fourth order, together with Fabry and Perot's lines at $\lambda = 4736$ and 4859 in the third order. The wave-lengths of the last two lines were thus determined direct, with one intermediate stage, from Fabry and Perot's lines at $\lambda = 5302$ and 5434. The wave-lengths, as determined by the grating, however, did not agree with the values found by the interference comparison; for example, Kayser found the wave-length $\lambda = 4736{\cdot}804$, instead of Fabry and Perot's number $\lambda = 4736{\cdot}785$. As the individual grating measurements agreed to 0·003 A. it is clear that either the coincidence method is unsound, or that Fabry and Perot's values are wrong. With the second grating, proceeding in exactly the same way, a discrepancy of 0·108 A. was obtained between the grating coincidence and the interference value. The two gratings were then compared directly together. With each grating two plates of the region $\lambda = 5302$ to $\lambda = 5434$ in the second order were taken, and the third order lines were measured. Whilst the two plates taken with each grating agreed to within 0·003 A. there was a constant difference of 0·03 A. between the values found with the two gratings. Kayser, therefore, concluded that there is no reason to doubt Fabry and Perot's values, but that the method of coincidences is not applicable at any rate for his gratings. As the result of this criticism by Kayser the coincidence method has by common consent been abandoned.

Mounting of the Concave Grating (Eagle's Mounting).—This method of mounting the concave grating, as already explained on p. 166, is of the Littrow type, that is to say the incident rays and the diffracted rays make practically the same angle with the normal, with the result that the latter return along almost the same path as that of the former. It has many great advantages over the Rowland method, and there is little doubt that these more than outweigh the minor disadvantages and that for general use it is far superior to the older mounting.

In order to secure the best definition with the concave grating it is necessary that the slit and grating be situated on the circle described on the radius of curvature of the grating as diameter, in which case all the spectrum lines are brought to a focus on the same circle. The distance, therefore, from the grating to the slit will, in this method of mounting, vary greatly with the angle of incidence, and thus the grating must be capable of considerable motion in the line of sight and also of rotation about a vertical axis. The only motion necessary for the camera is one of rotation about a vertical axis through the centre of the emulsion of the photographic plate.

The grating rests on a carriage which is mounted on rails and can be moved backwards or forwards by a worm gearing. The rails carrying the carriage and grating are mounted in a rectangular double-walled box, the space between the two walls being packed with slag wool to maintain constancy of temperature. At one end of the box is placed the camera, and at one side, near to the camera, is mounted the slit. The rays from the slit are reflected at right angles by a quartz right-angle prism mounted on a table which is carried on a pillar from the bottom of the box. The rays fall on the grating and the diffracted rays return along the same path, but, by reason of a slight tilt of the grating, a little above the incident rays, so that they pass above the right-angle prism, and they then are brought to a focus on the photographic plate. The two motions of the grating are operated by long rods which project through the end of the box under the camera. The apparatus is shown in Fig. 103. Eagle gives the following account of the method of adjusting and focussing the instrument.[1]

An arc lamp is set up at a distance of some feet from the slit and in such a position that the light entering the slit is horizontal and at right angles to the side of the box. A lens is then introduced to throw an image of the arc on the slit. It has been found convenient to have this lens, which is an achromatic glass one of 2·5 inches aperture and 12 inches focal length, mounted on rails parallel to the path of the light and the arc lamp on rails at right angles to this. For ultra-violet work a concave speculum metal mirror of 2·25 inches aperture and 9 inches focal length is employed, as a quartz lens does not produce an achromatic image. This is also mounted on rails, and in using it the arc is placed sufficiently out of the line of collimation to prevent the direct light from the arc which enters the slit from falling on the grating.

The height of the lower edge of the slot in the camera face should be the same as that of the centre of the grating, and the top of the quartz prism should be slightly below this so as to permit of an unobstructed view of the grating from the slot. Care must be taken when the rails and carriage are fixed in the box that the axis about which the grating rotates is vertical. This can be tested by means of a small spirit-level placed directly on the worm wheel.

The position of the image lens having been fixed, the totally reflecting quartz prism is adjusted by tilting and rotating about the vertical sc

[1] *Astrophys. Journ.*, 31, 120 (1910).

that the reflected beam of light covers the grating symmetrically. The grating must now be levelled so that the spectrum is the right height in the field in all orders. This is readily done by first adjusting the two

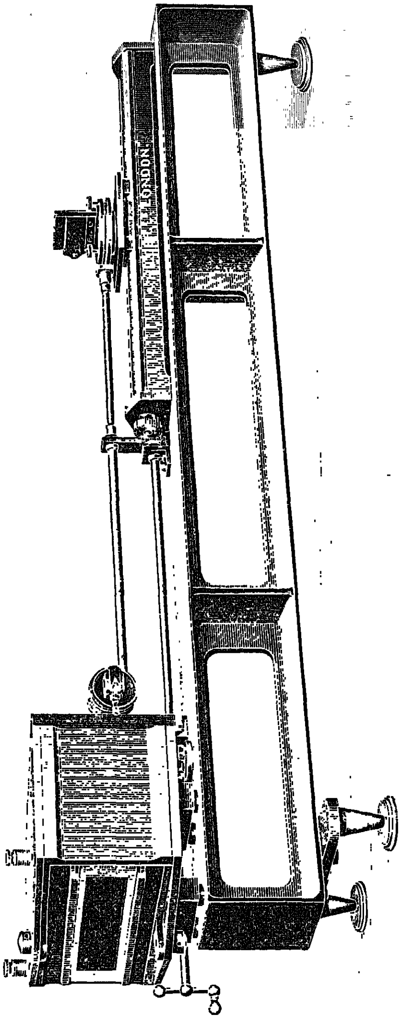


FIG. 103.

levelling screws behind the grating so that the spectra on each side of the normal are the same height in the eyepiece, and then adjusting the levelling screw in front till one of them is the correct height.

The instrument is focussed for photography as follows: The handle rotating the grating is turned till the required region is in the field of view. The grating is then advanced by means of the other handle till it is seen on observing the lines with an eyepiece that they are focussed in approximately the right position in the centre of the field. From the reading on the first handle when the central image is brought into the centre of the field of view, the inclination of the grating to the incident light can be found, the number of teeth on the worm wheel being known. The camera is then set to this inclination by means of its scale, the required scale reading being given by adding the reading for no swing to the product of the inclination of the grating in radians into the radius of the scale. The final focussing must now be done by photography. A series of half a dozen photographs are taken on a single plate, the grating being advanced by 0·05 inch between each successive exposure, the selected positions lying on each side of the approximate focus observed. The spectrum which shows the lines in the centre of the field in best focus gives the position of the grating carriage, whilst from the positions in which the ends of the plate are in focus the corrections to be made to the swing can be worked out. It must be remembered that the focus moves in and out twice as fast as the grating. If δ is the difference in focus between the centre of the plate and its ends, $2a$ its length, and r the radius of the scale recording the camera swing, the correction to be made to the scale reading is $\frac{r\delta}{a}$.

The three position readings together with the range of wave-length[s] obtained on the plate are then recorded, and to photograph any spectrum in this region in future, it is only necessary to set the three recorde[d] readings on their respective scales, when the instrument will be in focus A series of focussing plates as above are taken throughout the differen[t] orders and the results tabulated, from which in a few seconds the instru ment can be set in adjustment for any desired region.

A very convenient addition to this apparatus is a micrometer eye piece mounted on a board which fits into the camera like the dark slid[e] In using the eyepiece the camera is set at right-angles to the centr[al] diffracted ray from the grating. By turning the two adjusting handle the whole visible spectrum can be brought under view and examine[d] The value of one division on the drum of the eyepiece has a consta[nt] value in wave-lengths for any position in the spectrum of a given orde[r] From the general equation for reflecting gratings

$$n\lambda = b(\sin i + \sin \theta)$$

we have

$$Nn\lambda = \sin i + \sin \theta,$$

where N is the number of rulings per cm.

By differentiation

$$Nnd\lambda = \cos \theta d\theta = \cos i d\theta$$

since

$$\theta = i \text{ very nearly.}$$

If r be the distance from the eyepiece to the grating and ds be the apparent distance between any two lines in the eyepiece, we have

$$d\theta = \frac{ds}{r}.$$

Now $r = \mathrm{R}\cos i$, where R is the radius of curvature of the grating and hence

$$ds = \mathrm{RN}n d\lambda.$$

It follows that the scale in the eyepiece, $\frac{ds}{d\lambda}$, is constant throughout a given order. By the use of this eyepiece the difference in wave-lengths between close lines can be measured with a probable error of only 0·02 or 0·03 A. in the first order.

The Eagle mounting possesses the following advantages over the Rowland mounting.

1. The very small space occupied.
2. No darkened room is necessary.
3. It is very much cheaper than the Rowland mounting.
4. Spectra on either side of the normal may be used with equal facility, a point of some value, as it may happen that the better third order spectrum is on the opposite side to the better first order spectrum.
5. Everything being on the same axis, great rigidity is obtained. External vibrations tend to shake the instrument as a whole rather than one part with respect to another, and consequently are less liable to affect the definition.
6. A slightly increased dispersion is obtained. The dispersion in the Rowland mounting and in the eyepiece of the Eagle mounting is given by

$$\frac{ds}{d\lambda} = \mathrm{RN}n.$$

Since, however, the photographic plate is inclined at an angle i, the scale on the plate is

$$\frac{ds}{d\lambda} = \frac{\mathrm{RN}n}{\cos i},$$

but there is no corresponding increase in the resolving power.

7. Higher orders can be obtained than with the Rowland mounting.

Since
$$\mathrm{N}n\lambda = \sin i + \sin\theta \text{ and } \theta = i,$$
$$\lambda = \frac{2\sin i}{\mathrm{N}n}.$$

Hence the same wave-length can be obtained with $i = 30°$ as with grazing incidence in the Rowland mounting where $\theta = 0$. The value of these higher orders is very great, and Eagle says that in a photograph

of the head of the cyanogen band at $\lambda = 3883$, taken in the fifth order with a forty-minute exposure, lines only 0·05 A. apart were distinctly resolved. With a grating 100 cm. radius and 14,400 lines to the inch, the following regions can be obtained:—

First order	Extreme	Ultra-violet	to	26,000 A.
Second order	,,	,,	,,	13,000 A.
Third order	,,	,,	,,	8,700 A.
Fourth order	,,	,,	,,	6,500 A.
Fifth order	,,	,,	,,	5,200 A.
Sixth order	,,	,,	,,	4,300 A.

8. The steadiness of the temperature, which is a point of most vital importance. In one case a twenty-eight hours exposure was given for the first order spectrum of the hydrocarbon bands of the flame of a Mecke burner. On the photograph, lines 0·15 A. apart were distinctly resolved. Since the theoretical resolving power was 0·11 A., the temperature must have remained constant within 0·5°, even though the external temperature varied very considerably.

9. The decreased astigmatism obtained has already been dealt with on p. 167.

10. Owing to the fact that the grating is used at the position of minimum deviation the definition is better than with Rowland's mounting, but since the path errors are very small in either case, the point is not perhaps of much practical importance. It can be shown[1] that if the light be incident at an angle i on a truly spherical concave grating, the path error of the light which falls on the sides of the grating over that which falls on the centre will be

$$\frac{b^4}{8R^3} \sin i \,.\, \tan i,$$

where $2b$ is the breadth of the ruled space and R is the radius of curvature. In Rowland's mounting there is no path error in the diffracted light, hence the above expression gives the total path error. In the Eagle mounting, since the light returns along the line of incidence, the path error will be twice that amount, but since the same spectrum line is obtained with half the value of sin θ and therefore with less than half the value of tan θ, the path error for the same lines is less than half what it is in Rowland's case.

The Eagle mounting has the apparent disadvantage compared with the Rowland mounting in that it does not remain in automatic focus. The difficulties in obtaining the correct adjustments for focus are no greater, however, and once the series of focussing plates has been taken, the trouble of focussing the instrument for any of these regions is practically nil, since it is only necessary to set three known readings on their respective scales. If the regions of the focussing plates have been

[1] Schuster, *Optics*, p. 121.

carefully chosen it will be seldom that a region not coinciding with one of them is required.

The more obvious disadvantage of this mounting, namely, that the spectra photographed are not truly normal, is more apparent than real.

The greatest deviation between the true wave-length and that calculated from a linear interpolation formula taken over a 3-inch range in the green of the first order is only 0·2 A. Such a deviation makes it generally practicable to employ a simple linear interpolation formula between two standards and to draw a curve of errors showing the differences between the calculated and the true wave-lengths on intermediate standard lines. From this curve the corrections to be added to the unknown wave-lengths can be determined. In all cases of the determination of accurate wave-lengths, even when using a Rowland mounting, such a curve of errors should be constructed, if only to detect and eliminate accidental errors of setting on the standard lines from which the equation is calculated. So far then the fact that the spectrum is not normal makes no difference whatever.

When, however, it is required to obtain a uniform reduction over a much longer range it is best to use a formula of the type

$$\lambda = a + bs + cs^2,$$

which represents the spectrum with the same accuracy as it is represented by a linear formula in Rowland's case.

Let λ_1, λ_2, λ_3 be the wave-lengths of three lines from which it is required to determine the constants of the equation and s_1, s_2, s_3 their respective scale readings, of which the second should be about midway between the first and third. The following solution is perhaps the most convenient to use:—

$$\lambda = \left[a - \frac{e}{4}(s_1 - s_3)^2\right] + bs + e(s - s_m)^2$$

where

$$b = \frac{\lambda_1 - \lambda_3}{s_1 - s_3},$$

$$a = \lambda_1 - bs,$$

$$e = \frac{\lambda_2 - a - bs_2}{(s_2 - s_1)(s_2 - s_3)}$$

and

$$s_m = \frac{s_1 + s_3}{2}.$$

In this form the constants are adapted for logarithmic calculation.

Since the light rays in the Eagle mounting do not fall normally on to the photographic plate, care must be taken only to use good quality plates or films. If i be the angle of incidence, a local depression of depth h will displace a line happening to fall in it by $h \tan i$. Such displacements are revealed by the curve of errors and are of course not peculiar to this instrument but are common to all those in which the plate is considerably inclined to the light rays.

Interpolation Method of Measurement of Wave-length with the Concave Grating.—The present method of measurement of wave-lengths, except of course those of secondary standards, resolves itself into a comparison between known and unknown, carried out very similarly to that already described in Chapter V. for prism spectrographs. For this purpose either Rowland's or Eagle's mounting for the grating may be employed but there is little doubt that the three great advantages of the latter, namely, cheapness, rigidity, and constancy of temperature render it far preferable to the former.

As regards the standard of comparison to be adopted, it is necessary for work of the highest accuracy to use the iron arc spectrum, supplemented in the orange and red by the neon spectrum, but as was explained on p. 138 other spectra may be used as standards if such great accuracy is not required.

In order to obtain the comparison photographs, it is to be recommended that the two spectra, known and unknown, be perfectly superposed upon one another to ensure the greatest possible accuracy. This is simple enough when arc spectra are to be measured, because one pole of the arc may then be made of iron, and the other pole of the substance the spectrum of which is to be measured. When the spectrum of this compound arc is photographed, it stands to reason that the two sets of lines are correctly placed with regard to one another. In the case of other types of spectra, such as spark spectra or those of rarefied gases, the two spectra must be photographed separately, and in this case great care must be exercised in order to obtain their relative positions quite correct. The chief point to be secured is that the whole of the grating be illuminated with the incident light, and for this purpose a condensing lens should be used to focus an image of the light source upon the slit.

The following method of procedure may be adopted. The iron arc is first put in such a position that the condensing lens (which must, of course, be made of quartz) can focus an image of it upon the slit. The slit is now opened and the lens taken away; then the arc is moved from side to side until it is found that the grating is illuminated in the centre. This is readily enough seen by looking through the camera at the grating with the naked eye, standing far enough back to focus the narrow spectrum produced. The slit is then closed to the working width, and the lens put in place, so as to focus an image of the arc on to the slit; it is then securely clamped in position. A plate is then put in the dark slide, and the latter fixed in position to the camera back, and a photograph taken. When the correct exposure has been given, without disturbing any part of the grating mounting, the arc is moved, and the second source of light put in place, so that its image is focussed on nearly the same part of the slit as was the image of the arc before, this being done without moving the condensing lens. The exposure of this spectrum is thus started, and when finished the plate will carry the two photographs quite correctly superposed, provided no shifting of the camera took place during the process. If due care be taken, there will

e no need to expect this, but it is better that the unknown spectrum ontain some lines the wave-lengths of which are well known, to serve s a check against any possible shifting of the apparatus; if the wave-ngths of these lines found from the measurements of the photographs gree with the known values, then the relation between the spectra may e assumed to be quite accurate.

The temperature is an important factor in an accurate comparison etween two spectra. A change of temperature can easily produce a erious error, owing more particularly to the expansion or contraction of ne grating, and the consequent change in the grating space. It is bsolutely necessary that the temperature be kept constant during the xposures, for the errors that may creep in are surprisingly large. The nange in the wave-length is proportional to the change in the grating pace produced by the temperature variation, for we have $\frac{d\lambda}{\lambda} = \frac{db}{b}$, here b is the grating space. Now $\frac{db}{b}$ is about 0·00002 for a change of ° C., hence in the first order, when $\lambda = 5000$, $d\lambda = 0{\cdot}1$ Ångström. ince a full-sized Rowland grating with 14,438 lines to the inch will esolve spectrum lines 0·13 Ångström apart, so a temperature change of ° C. will make it impossible to resolve lines less than 0·23 Ångström part. In the second order the variation in the position of the lines ill be twice as great, and such a creep of the lines during the exposure ill make any accurate measurements impossible even in the first order.

It must be remembered that, unless absorbing screens are used, pectrum lines will be found to be present belonging to different orders om the one chosen. In view of the failure of the theoretically correct iperposition of different orders it is necessary only to compare lines, nown and unknown, in the same order. Care must be taken therefore recognise the lines due to the orders not required, in the case of both ne standard spectrum and the unknown spectrum. A photograph of ach may be taken separately, both with and without absorbing screens, nd a comparison of these, each to each, will at once enable the lines of ne chosen order to be identified. Finally, a comparison of the plate, n which both known and unknown spectra have been photographed, ith those plates taken separately will render it possible to pick out and lentify the secondary standards and unknown lines, both of which have be measured. It will be found a great convenience to rule a fine raight line with a needle along the whole photograph through the entre of the spectrum. Where the various lines, which have been icked out, cross this ruled line, they are marked, the two lines in dis-nctive ways, *e.g.* the standard lines may be noted by a fine black ink ıark, and the unknown lines by a similar red mark. This is simply for ne purpose of recognising these lines when measuring the plate, for the eld of view of the measuring instrument is always very small, and unless ne marks are made close to the part measured they will not be seen.

The photograph is now ready to be measured and for this purpose ither the stereo-comparator or travelling micrometer may be used.

The measurements are all referred to two standard lines, one at each end of the region selected on the plate, and great care must be taken that the plate is correctly oriented with regard to the measuring instrument. The fine ruled line should be in the field of view and, further, in the case of the travelling micrometer the direction of travel must be exactly at right angles to the spectrum lines and one of the cross-wires in the eyepiece should be parallel to them. Care must also be taken to guard against the backlash in the screw of the micrometer by always approaching every line from the same side, namely that nearest the starting-point. All the marked lines are measured, both known and unknown, care of course being taken to distinguish between them.

The wave-lengths of all the lines are then calculated by simple proportion between the wave-lengths of the two extreme standard lines. The calculated wave-lengths of the secondary standards are then compared with their known wave-lengths, and the differences found are plotted on squared paper against their scale readings and a curve of errors drawn through the points so obtained. In the first place, the smoothness of this curve and the general lie of the various points in relation to it will give at once a measure of the accuracy of the determinations, and complete confidence can only be felt therein when a smooth curve is obtained. For this reason it is necessary to draw this curve even when Rowland's mounting is used and the spectra are normal, as otherwise no indication is at hand of the accuracy of working. In the second place, from this curve of errors the corrections can be read which must be applied to the calculated wave-lengths of the unknown lines in order to obtain their true wave-lengths. This method of work eliminates almost all errors in the measurements of a given plate, because such will be revealed by the general shape of the curve. There are two possible errors, however, which cannot be eliminated from the measurements of a single photograph. The position of an unknown line may be wrongly measured by accident—such a mistake in the position of a standard line will at once be recognised from the curve. Again, owing to a flaw in the photographic plate, such as a depression in the emulsion, a line may be displaced from its correct position in the photograph, if the photographic plate is set at an angle to the path of the rays, as is the case in Eagle's mounting. These last two possible errors can only be detected by the measurements of several photographs of the same region of the spectrum. In each case the same procedure is adopted and the various determinations of the wave-length of each unknown line are compared together. If there is no reason to doubt the inherent accuracy of any of these, the mean of them all will have the greatest probable accuracy. If any value differs markedly from the others it should be rejected.

This method has already been described in Chapter V., p. 149, for prism spectrographs and it is repeated here for the sake of continuity. The intensities of spectrum lines and their assessment or measurement were also dealt with in the same chapter, p. 145, and need not here be discussed.

There is one possibility which is more likely to arise in the case of ɔmparison photographs taken with a concave grating than in the case ˋ those taken with the prism instruments. It may happen that the ave-length of one of the unknown lines is very nearly equal to that of ie of the standard lines and that the intensity of the latter is much eater than that of the former. If the two spectra are exactly superɔsed, the former line may be partly or wholly obscured with the result at its accurate measurement becomes impossible or at any rate very icertain. This difficulty may be surmounted, when the comparison iotograph is being taken, by arranging that the images of the two urces, known and unknown, fall on the slit, one a little above the her. The two spectra will then overlap without being exactly superɔsed and any closely situated lines will be detected.

The reason why this difficulty is more likely to arise with a concave ating than with a prism instrument is the astigmatism of the former. ith a prism spectrograph the overlapping of two spectra does not ccur unless care has been taken to secure it by arranging that the iages of the two sources, the spectra of which have to be compared, e superposed on the slit. In the case of a concave grating, especially ith Rowland's mounting, where the astigmatism is very great, it often ecomes impossible to photograph the spectra of two sources without ɔmplete superposition. In such cases the use of the Rowland diairagm shown in Fig. 89 is to be recommended.

There remains one final point to be mentioned, which arises om the great differences sometimes to be found in the intensities of ie various lines in a given spectrum. When a photograph is taken of spectrum with a short exposure, the stronger lines will appear very iarp and well defined whilst the weaker lines will not possess sufficient tensity for their measurement. On the other hand, a longer exposure, ade for the purpose of increasing the intensities of the weaker lines, ay cause the stronger lines to appear broad, owing to halation, and ɔnsequently less easy to measure accurately. The correct period of kposure and time to be given in the developing bath are matters which in only be learned by experience with each individual apparatus. It ay be found advisible, and it frequently is advisable, to take several ates for each region of wave-lengths with different times of exposure,) that both the stronger and weaker lines can be measured under the est conditions.

CHAPTER VIII.

THE EXTREME INFRA-RED AND ULTRA-VIOLET REGIONS OF THE SPECTRUM.

As was described in Chapter II., the existence of the infra-red region was discovered by Sir W. Herschel in 1800, who, in testing the heating power of the different colours of the spectrum by placing a very sensitive thermometer in the path of the various rays, found that the heat intensity increased towards the red end, and finally reached a maximum at a point some distance beyond the end of the visible portion. It was Ampère, in 1835, who first concluded that these heat rays were of the same nature as the light rays in the visible portion of the spectrum, that they were both due to waves in the same medium, and only differed from one another in their wave-length. In 1840 Sir J. Herschel succeeded in proving the existence of Fraunhofer lines in this region of the solar spectrum, by projecting it upon a strip of dull black paper, moistened with alcohol. Had the spectrum been perfectly continuous, it is evident that the increase of temperature produced by the rays would have caused the alcohol to evaporate equally from those portions of the paper covered by the heat spectrum. In actual fact he found that this was not the case, but that damp spots were left in places, which fact clearly pointed to the existence of absorption bands in the solar spectrum.

In 1880[1] Abney published a map of the infra-red region of the solar spectrum from $\lambda = 7160$ to $\lambda = 10{,}000$ Ångströms, which he had obtained by photographic processes, with the help of gratings and prisms. The complete description of the method Abney employed in the preparation of the photographic plates sensitive to this region will be given at length in Volume II., Chapter III.; suffice it, therefore, to say here that the ordinary silver bromide emulsion appears red by transmitted light, and is, therefore, readily absorbent of the blue rays. Abney succeeded in the preparation of an emulsion which was blue by transmitted light, and which, therefore, absorbed the red rays. He found that such emulsions were sensitive to as far as wave-lengths of 20,000 A. The process of preparing the plates for this work is very troublesome, and as they very soon lose their sensitiveness to the red rays, this method of investigation has found very little application since the brilliant work of Abney himself. At the present time there are known methods of dyeing photographic plates in order to render them

[1] *Phil. Trans.*, **171**, I., 653 (1880); and also **177**, A., 457 (1886).

sensitive to the red end of the spectrum, and, indeed, there are upon the market certain brands of plates especially made for work in this region. Under certain circumstances it is possible to reach $\lambda = 9000$ A. by means of such plates. By use of what is known as the phosphoro-photographic method, it has been found possible to obtain photographic records of emission spectra to as far as $\lambda = 20{,}000$ A.

With the exception of the photographic methods, all the modern methods of investigation into the infra-red depend on the use of instruments capable of directly recording the intensity of the radiant energy they receive. By means of the apparatus now employed it has been found possible not only to penetrate an extraordinary distance into the long wave infra-red region, but also in the shorter wave region to detect minute variations in the intensity of the radiations, with the result that both fine-line emission and fine-line absorption spectra have been recorded with extraordinary accuracy. The pioneer investigations into this region have been undertaken in several directions by independent workers, and it may now be said that the technique has become so well worked out that during the past few years this field of work has almost passed out of the hands of the specialist and become open to any who desire to enter it. It is obvious that the original work in this region presented at first many difficulties. Nothing was known of the behaviour of substances towards the long waves, nor of their indices of refraction, nor were any methods developed for measuring the wave-lengths of the radiations, the whole being completely new ground. Step by step, however, advances were made and landmarks established in the way of definite radiations of known wave-length characteristic of substances. These are now at the services of every experimenter, who can make use of them for calibrating his apparatus, with the result that modern work has become largely a matter of interpolation between these.

The most recent results would seem to show that quite apart from its intrinsic interest investigation of this region holds out very great promise. At the present time the fascinating work based on the Bohr theory of the atom and the modern developments of X-ray spectroscopy have tended to focus the attention of scientific workers on to the most refrangible end of the spectrum, but I firmly believe that the time will soon come when the long-wave region will equal the short-wave region in interest. It has been shown that all substances possess powers of selectively absorbing infra-red rays to as far as $\lambda = 3000\mu$, and the integral relations between the many long wave radiations selectively absorbed by a substance seem to prove that they are inherently characteristic of atoms and molecules. Up to the present no direct connection has been found between these very small frequencies and the very large frequencies dealt with in the Bohr theory. This connection will doubtless soon be discovered and I am brave enough to prophesy that the key to the problem of the absorption and radiation of energy by elementary atoms will be found in the infra-red. It is hoped that more workers will enter this field and take a hand in unravelling the mysteries that still lie hidden therein.

It may be said that the pioneer investigations into the infra-red were of four kinds. First, the extension of the solar spectrum and the measurements of the wave-lengths of the Fraunhofer lines in this region. Second, the investigation of the indices of refraction of various media for rays of long wave-length. Third, the identification by emission and absorption spectra methods of the radiations specifically characteristic of substances. Fourth, the determination of the distribution of energy in the emission spectrum of an absolutely black body.

Without entering fully into the methods of work, it is necessary to give a brief account of the original means employed to determine the position which a particular ray occupies in this region, that is to say, the first methods adopted to calibrate this region in terms of wave-lengths. When gratings came to be used as the dispersing apparatus, the determination of the wave-lengths from the angles of diffraction was simple enough, but in the use of prism apparatus there was no guide whatever to the wave-lengths, since it is clearly impossible to extrapolate on a dispersion formula.

In the latter case interference bands have been used, by counting which one can readily tell how far one is progressing into the unknown region. These were first made use of by Fizeau and Foucault [1] in 1847. Mouton, in 1879, published an account of some measurements of the wave-lengths of the long-wave rays, in which he employed these interference bands. These bands were produced in the following way.[2] A quartz plate, cut parallel to its optic axis, is put between two Nicol prisms and perpendicular to the path of the light; the principal section of the quartz plate, makes, therefore, an angle of 45° with the principal sections of the Nicols. Under these circumstances two interfering components are obtained, with a difference of phase which is equal to $\frac{e(\mu_e - \mu_0)}{\lambda}$ where e is the thickness of the plate, μ_e and μ_0 the indices of the extraordinary and the ordinary rays respectively, and λ the wave-length. When this expression equals $\frac{2k + 1}{2}$, k being some whole number, then a black band will be produced. As k represents the order number of the fringe, it is only necessary to know it for one fringe, when it will be known for all, as it changes by one from fringe to fringe. From the above relation the wave-length corresponding to any band can be found from the equation—

$$\lambda = \frac{2e(\mu_e - \mu_0)}{2k + 1}$$

if e, k and the indices of refraction are known.

It is clearly impossible to measure e by ordinary methods, and it is, therefore, necessary to use optical means. This Mouton effected by allowing the light from the last Nicol to fall upon the slit of a spectrometer

[1] *Comptes Rendus*, **25**, 447 (1847).
[2] *Ann. Chim. Phys.* (5), **18**, 145 (1879).

provided with a grating, and by measuring the deviations produced for two bands, and from his knowledge of the wave-lengths corresponding, he was able to calculate the values of e and k. In order to do this it was necessary to know the values of $\mu_e - \mu_0$ for the wave-lengths dealt with; these were obtained from an interpolation formula derived from the well-known Cauchy dispersion formula—

$$\mu_e - \mu_0 = \alpha + \frac{\beta}{\lambda^2}, \text{ where } \alpha = 0{\cdot}0088205 \text{ and } \beta = 0{\cdot}0001093.$$

These constants were obtained from observations in the visible region, and cannot be used for extrapolation into the infra-red. When the

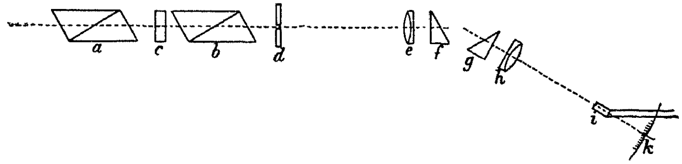


FIG. 104.

values of e and k had been obtained, it became simply necessary to measure $\mu_e - \mu_0$ for the interference bands in the infra-red, from which the wave-lengths corresponding could be obtained at once. This Mouton carried out by means of an ordinary spectrometer, provided with a Thollon prism pair; a diagram of his apparatus is shown in Fig. 104. a and b are the two Nicols, and c the quartz plate; d is the slit of the spectrometer, f and g the prism pair, and i a delicate thermopile placed in the focus of the telescope lens. By means of the thermopile the positions of the black interference, or "cold," bands in the heat spectrum are detected. The rest of the apparatus explains itself.

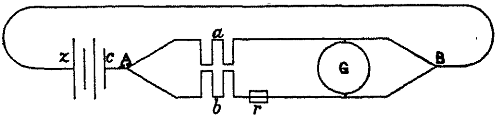


FIG. 105.

In 1881 was published the first notice of Professor S. P. Langley's bolometer,[1] which was an exceedingly great advance upon any of the apparatus which previously had been used. This apparatus, which Langley called the actinic balance or bolometer, consists of an electrical resistance thermometer—that is to say, an instrument which measures temperature in terms of the change of electrical resistance of a very fine strip of metal. The elementary theory of the instrument is as follows:—

The current from a battery divides itself at A (Fig. 105) into two

[1] *Amer. Journ. Science* (3), **21**, 187 (1881); *Chem. News*, **43**, 6 (1881); *Ann. Chim. Phys.*, **24**, 275 (1881).

portions, one of which passes through a long bent strip of metal at *a*, and the other through an exactly similar strip at *b*; they both join at B and return to the battery. Evidently if the resistance of the two arms be equal, equal quantities of current will travel along each, but if the resistance of one be greater, less current will flow along that arm, and, consequently, a certain amount will flow through the galvanometer G, an amount directly proportional to the difference of resistance between the two arms. If now *a* and *b* be made of exactly the same length of similar strip, then their resistance will be the same when at the same temperature; in actual practice this is often not absolutely secured, and a resistance box is introduced at *r*, to compensate for the slight difference in *a* and *b*, and also in the resistance of the two arms as a whole arising from slight differences in the two leading wires. Let us suppose now that the two strips *a* and *b* are at exactly the same temperature, and the resistance of the two arms absolutely equalised, then no current will flow through G; if, however, either *a* or *b* be heated, its resistance will at once increase, and the balance will be destroyed, with the result that the galvanometer needle will be deflected

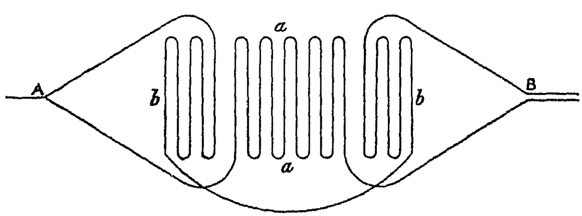


FIG. 106.

by an amount proportional to the difference in temperature between *a* and *b*. In practice *a* and *b* are both brought close together, so as to secure their both being affected equally by change of the room temperature; one alone is exposed to the radiation, the other being screened. The arrangement of the strips is diagrammatically shown in Fig. 106, there being an equal number of strips in *a* and *b*, with half of those of *b* set on each side of those of *a*. These strips, which were made of very thin steel or platinum, are arranged, according to the diagrams, upon ebonite frames, shown in Fig. 107, and these frames are mounted in a wooden or ebonite tube, as shown in Fig. 108 at B.

The arrangement of the strips upon the frames will be seen quite clearly from Fig. 107, where they are shown by the dotted lines. The central set of strips on each frame form one arm of the balance, and the outer sets form the other arm. The upper ebonite frame exactly fits upon the lower, and the strips upon each frame are so placed when the two discs are fitted together that those upon the one disc lie in the spaces between those upon the other disc. This arrangement is adopted in order to expose as much surface of the strips to the radiation as possible. The two discs fixed together are mounted in an ebonite or

wooden tube, as shown in B, Fig. 108. A screen, K, is mounted in the tube just in front of the discs, in order to protect the outer sets of strips from the radiation; diaphragms, as shown at SS, Fig. 108, are fixed to minimise the air currents inside the tube.

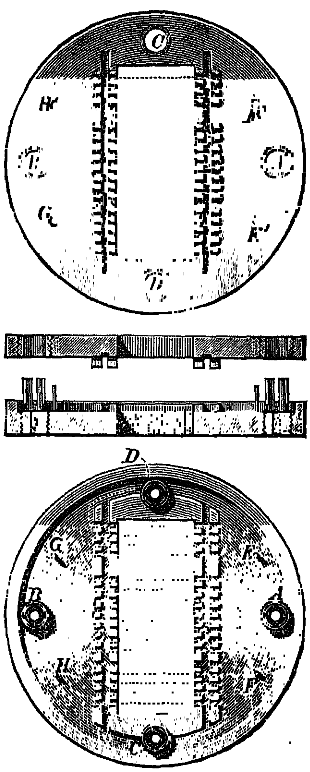


FIG. 107.

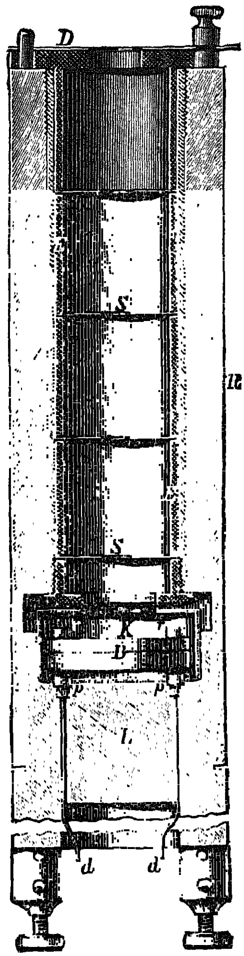


FIG. 108.

The apparatus shown in Figs. 107 and 108 is an old form; the design most recently employed by Langley is too complicated for reproduction on a small scale.[1] It may be pointed out that when the

[1] *Annals of the Astrophysical Observatory, Washington*, vol. i.

bolometer is in use a current of electricity is continually flowing through the arms, the amounts flowing through each arm being exactly balanced when at the same temperature.

The instrument described here is known as a surface bolometer—that is to say, one which exposes a considerable surface to the radiation; such an instrument is of no use for the measurement of spectrum lines. In this case the sets of strips as depicted above, are replaced each by one or more strips, mounted upon their edges so as to form a very narrow line, and expose as narrow a surface as possible to the radiation. The smaller the angular magnitude of the exposed strip, the more accurate will be the determinations of the position of spectrum lines. With the earlier forms of this apparatus Langley was able to measure a rise of temperature of 0·00001° C., and in his later apparatus he reached a sensitiveness of 0·000001° C. In the final form only one strip was exposed, which was 0·5 mm. broad and 0·002 mm. thick.

With these bolometers Langley investigated the heat spectrum of the sun, and at first measured the absorption caused by the earth's atmosphere. This was carried out by making observations with the sun high and low in the sky, and also by transporting the whole apparatus to a station on Mount Whitney, nearly 15,000 feet high.[1]

The first observations of the infra-red spectrum were made with the help of a flint glass prism as the dispersing apparatus, and a map of the new region was published,[2] in which the abscissæ were proportional to the deviations produced by the prism. In order to determine the wave-lengths of the absorption bands on this map the following device was adopted:[3] the rays from the sun were first diffracted by a grating and then refracted by a prism, and in this way the indices of refraction for rays of known wave-length were obtained; further, the prism served to separate the various superposed orders of spectra produced by the grating. A diagram of the apparatus is shown in Fig. 109. A beam of sunlight from a heliostat falls on to the concave mirror M, which focusses it upon the slit S_1 of a concave grating apparatus. This slit is protected from the great heat by a plate of iron, pierced with a hole, which is only a little larger than the slit. From the slit the rays fall upon the concave grating G, which focusses the spectral rays, as is known, on the dotted circle. At S_2, where the photographic plate, or eyepiece, is usually placed to observe the normal spectra, there is a second slit, which forms part of a prism spectrometer, of which the lenses are shown at L_1 and L_2, and the prism at P. The second lens focusses the image of S_2 upon the bolometer at B; the arm carrying the bolometer rotates round a centre under the prism, and there is an arrangement for always keeping the latter in the position of minimum deviation. The readings of the angle of deviation produced by the prism could be read accurately to 1′ of arc. The grating was one ruled by Rowland, with 18,050 lines, 142 to the millimetre, on a spherical mirror of 1·63 metres focus.

[1] *Nature*, 26, 314 (1882); *Brit. Ass. Rep.*, 1882, p. 459.
[2] *Phil. Mag.* (5), 15, 153 (1883). [3] *Ibid.* (5), 17, 194 (1884).

The method of experiment with the apparatus can be very shortly described, best in Langley's own words. "The apparatus having been previously adjusted, and the sunlight properly directed by the heliostat, the visible Fraunhofer line D_2 of the third spectrum of the grating was caused to fall upon the slit S_2 of the spectrobolometer. Then, according to the theory of the grating, there passed through this slit rays having the wave-lengths—

0·589μ, third spectrum,
0·888μ, second spectrum,[1]
1·767μ, first spectrum.

"The prism having been removed and the telescope brought into line, an image of S_2 was formed in the focus of the objective, and, on testing with the bolometer, the face of which was covered by a screen with a 2 mm. slit, a deviation of the galvanometer needle of 30 divisions was produced. The prism was then replaced, and then the angles of deviation were sought for the three rays. The first, *i.e.* D_2, gave a deviation of 47° 41′, and the third was found by turning the bolometer little by little about the position where the ray was expected, until the maximum heat effect was obtained. The slits were then narrowed in order to increase the accuracy of reading, and finally, the deviation for the ray $\lambda = 1·767\mu$ was found to be 45° 10′.

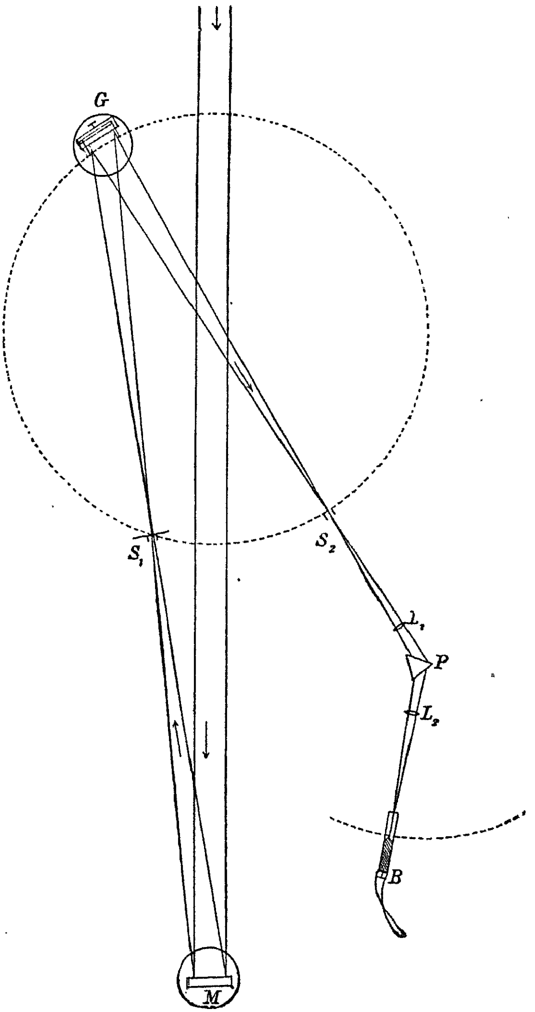


FIG. 109.

[1] In Langley's paper this is given as 1·178μ in error.

Proceeding in this way the deviations were obtained for several different rays, and a curve of dispersion constructed for the prism."

In a first investigation with this apparatus Langley carried his measurements to the limit $\lambda = 2 \cdot 03\mu$. After this work the apparatus was greatly improved in many ways; greater sensitiveness was obtained in the bolometer and galvanometer, and also the prisms and lenses were made of rocksalt, which eliminated the absorption exercised by the glass.

In a later investigation[1] upon the solar and lunar infra-red spectra, Langley found that the limit of the former was practically at $\lambda = 5\mu$, but that he was able to trace it to an estimated limit of $\lambda = 18\mu$. It is probable that the energy in this part of the sun's spectrum is strongly absorbed by the atmosphere. In the moon's spectra the chief maximum lies between $13 - 14\mu$, and from these and other observations Langley estimates the temperature of the moon in sunshine to be not more than $0°$.

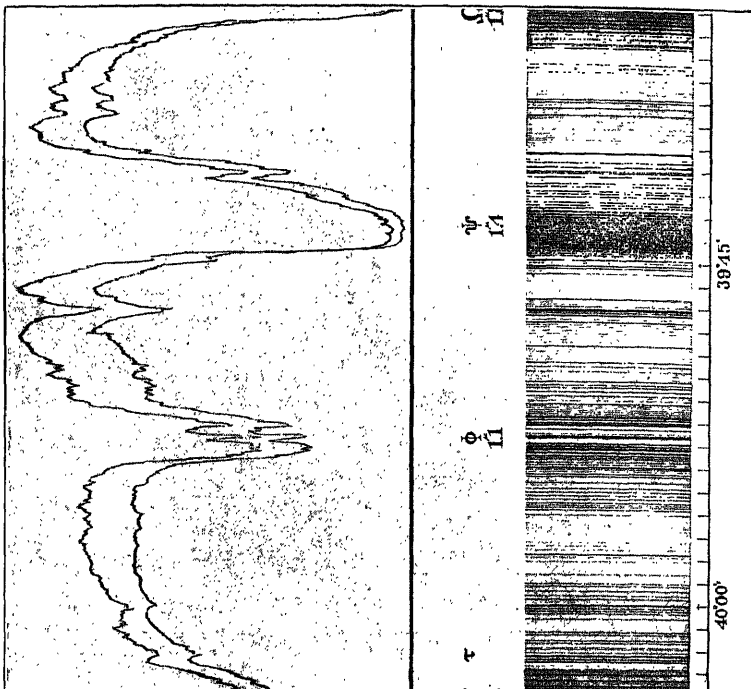
In his final work upon the solar spectrum, Langley made use of a new apparatus[2]; the light from a 20-inch siderostat passed through the slit of a horizontal collimator, which possessed a lens of rocksalt 17 cms. clear aperture, and 10 metres focal length. This lens focussed the ray upon a prism or grating; the prism was of rock-salt, and was 18·5 cms. high and 13 cms. deep in the face, and had a refracting angle of 60°. The angular width of the bolometer thread was decreased to $2''$ of arc by using a telescope lens of 5 metres focus; the sensitiveness was thereby increased, and by improvements in the galvanometer the apparatus was made capable of detecting a temperature change of 0·000001° C. The whole spectrometer was of the fixed-arm type, and the spectrum was made to pass over the bolometer strip by rotating the prism. An automatic self-registering method was adopted of recording the galvanometer readings. The spot of light reflected from the galvanometer mirror was focussed upon a broad strip of photographically sensitive paper. This paper strip was caused to move slowly in a vertical direction, and in this way a faithful record of the excursions of the light spot was obtained. At the same time the prism was slowly rotated, and, therefore, this record clearly showed all the temperature changes of the bolometer as the spectrum passed over it. Further, the motions of the sensitised paper and the prism were exactly co-ordinated, so that the angular position of the prism corresponding to any portion of the galvanometer record could at once be obtained. In this way, since the dispersion of the prism was already known, the wave-length of any spectrum line shown upon the record could be found, and also, from the length of the throw of the light spot, its intensity estimated. The delicacy of this apparatus was sufficient to show the D lines widely separated, with the nickel line in between; a diagram of a portion of the bolograph record is shown in Fig. 110, which is reproduced with Professor Langley's permission from the *Annals of the Astrophysical*

[1] *Phil. Mag.*, **26**, 505 (1888); and **29**, 31 (1890).
[2] *Brit. Ass. Rep.*, 1894, p. 465; and *Nature*, **51**, 12 (1894).

Observatory, Washington. By means of this apparatus Langley mapped the solar spectrum as far as $\lambda = 5{\cdot}5\mu$, and observed 700 lines between A and this limit.

Although for many years Langley was the only worker in this field, yet, before his final results were published, investigations had been begun and carried out by other experimenters, though not in the direction of the determination of the wave-lengths of the Fraunhofer lines. One of these was by Carvallo, on the dispersion of fluorite, under the title of *Spectres Calorifiques*, carried out during 1893 and 1894.[1] The chief interest of this paper lies in the improvement he introduced into Mouton's method described above. Mouton's method depended upon the use of the black bands in the spectrum produced, according to Fizeau and Foucault, with two Nicols and a quartz plate in between them; these black bands served the same purpose as the Fraunhofer lines in the visible spectrum, the indices of refraction being measured for the points of minimum intensity of the black bands. Carvallo found fault with the use of these points of minimum intensity, because the change of intensity at these places is very slow, and therefore the setting of the thermopile or bolometer is a matter of some uncertainty. It is preferable to use the regions where the rate of intensity change is the greatest, *i.e.* halfway between the centre of a black band and the centre of a bright band. At these places the difference of phase between the interfering rays is equal to a whole number of waves $\pm \frac{\lambda}{4}$. If now ϕ be the difference of phase, the intensity i of the spectrum can be found from the equation $i = \mathrm{I}\cos^2 \pi\phi$, where I is the intensity of the incident light. If now either the analyser or the polariser be turned through 90°, so that they become crossed instead of parallel, as they were in Mouton's case, then the intensity is complementary to i, and may be found from $i' = \mathrm{I}\sin^2 \pi\phi$. Carvallo bases two methods of experiment upon this; in the first of these he measures by the thermopile both i and i', one with the Nicols parallel, and the other with them crossed, and from these values finds the value of $\frac{i - i'}{i + i'}$, which it can be seen is equal to $\cos 2\pi\phi$. Now, when $\phi = k + \frac{1}{4}$, where k is the whole number of waves, then, of course, $\cos 2\pi\phi = 0$; by a series of observations, therefore, the deviation is found corresponding to $\frac{i - i'}{i + i'} = 0$, which is where the phase difference is equal to a whole number of waves $+ \frac{1}{4}$. In the second method the quartz plate and the analyser are set between the prism and the telescope, the analyser being so turned that its double refraction is utilised, and two spectra, one immediately above the other, are seen in the telescope; the intensity of one of the spectra is equal to i, and that of the other to i'. These two spectra are thrown upon the two arms of a differential thermophile, so that $i - i'$ is automatically measured by the galvanometer. As before, the position of the telescope is found corresponding to the

[1] *Ann. Chim. et Phys.* (7), 4, 5 (1895).


39°45'
40°00'
40°15'
0.92

condition that $i - i'$, and therefore also cos $2\pi\phi$, is equal to o. By this method the refractive indices of fluorite were measured between $\lambda = 1{\cdot}849\mu$ and $\lambda = 0{\cdot}39681\mu$ (H line).[1]

There are two names which will ever be associated with investigations into the infra-red, namely those of Rubens and of Paschen, for it is to their pioneer work that we owe so much for the development of the methods and for the valuable and important results which they have achieved. The work of these two scientists may be discussed separately even though their investigations have been concurrent.

In Rubens' first research[2] the indices of refraction of very many substances were determined with the help of a bolometer, interference bands being employed as landmarks, as in the case of Mouton's method. These were, however, produced in a different way; the light beam from an artificial source was reflected into the spectroscope from two parallel walls enclosing a thin layer of air, and in this way the interference bands were produced. The determination of the wave-length corresponding to the centres of these bands is rather simpler than it is in the case of Fizeau and Foucault bands used by Mouton. If m is the order number of a particular band, d the thickness of the air layer, and α the angle at which the air-plate is set to the incident beam, in this case 45°, then we have—

$$m\lambda_1 = 2d \cos \alpha = K$$

and

$$(m + 1)\lambda = 2d \cos \alpha = K, \text{ etc.}$$

By the observation of several bands in the visible spectrum it is possible to determine the values of m and λ for the bands, and also of the constant K. When the order number m is known for any one band, the numbers of all at once become known, as those of two consecutive bands simply differ by unity, and, of course, as one follows the bands towards the red their order numbers decrease. If now n be the order of the last visible band in the red, then the wave-length corresponding to the first band in the infra-red will be equal to $\frac{K}{n-1}$. The position of the bands was observed by means of a bolometer, two being used, which had a sensitiveness of $5 \times 10^{-6°}$ and $8 \times 10^{-6°}$ C., respectively. Rubens measured the dispersion of five crown and five flint glasses, differing in constitution amongst themselves, water, xylene, benzene, carbon bisulphide, quartz, rock-salt, and fluorite, to as far as $\lambda = 3{\cdot}0\mu$, when absorption begins; for the three last-named substances, the measurements reached $\lambda = 3{\cdot}5\mu$. The results of measurements of the dispersion of rock-salt, sylvin, and fluorite were published by Rubens and Snow,[3] in which the same apparatus and method were used but the bolometer was rendered more sensitive, the limit being reduced to $3 \times 10^{-6°}$ C. Rubens, in his next investigation[4] on the dispersion of fluorite, altered the experimental method and adopted that of Langley, viz. a grating and

[1] See p. 80.

[2] *Ann. der Phys.*, **45**, 238 (1892).

[3] *Ibid.*, **46**, 529 (1892).

[4] *Ibid.*, **51**, 381 (1894).

prism combined. Two gratings were employed, made of wire wound round a frame; in the one gold wire 0·0331 mm. in diameter, and in the other copper wire 0·0250 mm. was used.[1] These gratings were made in such a way that the space between two consecutive windings was exactly equal to the thickness of the wires, *i.e.* in grating No. 1 the grating space was 0·0662 mm., and in No. 2 it was 0·0500 mm. Under these circumstances (see Chapter VI., p. 158) the even orders of spectra are absent, and only the odd numbers are present, which are consequently brighter. With the two gratings mentioned, the fifteenth and the thirteenth orders respectively were very good. The bolometer was the same as used in the last research, and the measurements were taken as far as $\lambda = 6{\cdot}48\mu$.

In his next papers[2] Rubens extends his measurements, and shows the applicability of the Ketteler-Helmholtz dispersion formula; but, as the constants obtained in this formula were not the same as those calculated from some later measurements, they need not be more than mentioned in this place.

In order to understand the later work of Rubens, in which he deals with the dispersion of substances for heat rays of the greatest wave-length, it is necessary to discuss the research in which the existence of these rays was discovered and the method of dealing with them was worked out. In 1896 Nichols, in Ruben's laboratory, studied the reflecting power of different substances, especially quartz, and found that metallic reflection exists with the last for rays of about $\lambda = 9\mu$; the following brief description may be given of the apparatus employed. The rays from a Linnemann zircon burner were reflected from a polished plane surface of quartz, and were focussed upon the slit of a spectrometer by a rock-salt lens; a fluorite prism was employed as the dispersing apparatus, and for detection of the rays a radiometer was used. It may be mentioned that Rubens had already measured the dispersion of fluorite so that the wave-lengths of the rays dealt with could be found from the dispersion curve of this substance. The radiometer employed by Nichols in this work was a modified form of the instrument as originally devised by Crookes, in which mica vanes, accurately mounted upon a central spindle in vacuo, rotate when placed in the path of radiant energy. In Nichols's form[3] of this apparatus the mica vanes are suspended by a quartz fibre, and the angle through which they are turned from their position of rest is measured by the excursion of a spot of light reflected, as in the case of a galvanometer, from a very small mirror carried by the vanes. The following is a description of the apparatus which is shown in Fig. 111:—

The outer case consists of a bronze cylinder, A, bored out to within 5 mm. of the bottom; this cylinder is mounted upon a base provided with levelling screws. A glass cover, B, is ground accurately to fit the top of A, and a tube connects the apparatus through the stopcock H to

[1] *Ann. der Phys.*, **49**, 594 (1893).
[2] *Ibid.*, **53**, 267 (1894); and **54**, 476 (1895).
[3] *Ibid.*, **60**, 402 (1897).

an air-pump. At *g* is a small bridge, from which hangs a quartz fibre carrying the two mica vanes *a*, *a*; at *e* is a small mirror suspended from the vanes by a very narrow glass rod, *s*. The weight of the whole apparatus on the quartz fibre is only 7 milligrammes. There are two openings in A at *c*, *c*, one of which is provided with a brass tube closed with a fluorite plate through which the rays pass to the mica vanes; the other opening is closed with a glass plate, and serves to admit the light to illuminate the mirror at *e*.

The rays were allowed to fall upon one vane only, the other one acting as a compensator; the apparatus was so delicate that the energy from a candle 6 metres distant caused the deflection of the spot of light over sixty divisions on a scale placed $1\frac{1}{3}$ metres away. Nichols claimed that the radiometer has the following advantages over the thermopile and the bolometer. It is quite undisturbed by all magnetic and electrical influences. It can be better compensated against stray radiations, and, finally, it is free from disturbance due to air currents. Against it, however, may be urged that it is not as transportable as the bolometer or thermopile, and, further, all the rays examined must pass through the radiometer window, so that they suffer a certain amount of loss by reflection and absorption.

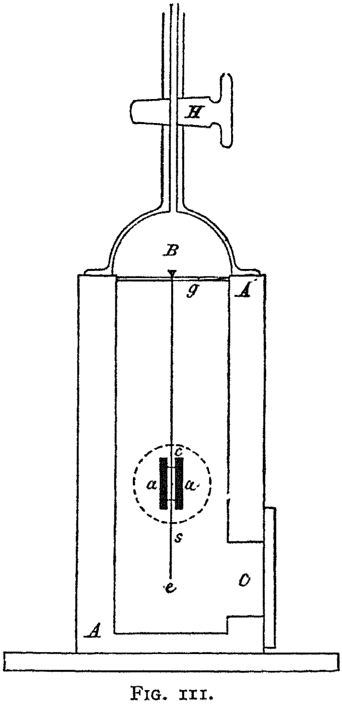


FIG. III.

In Nichols's apparatus an arrangement of mirrors was adopted, so that the telescope need not be moved, the spectrum being caused to pass in front of the slit by simply turning the fluorite prism. The wave-lengths of the rays were found from the deviation, using Paschen's values of the dispersion of fluorite.[1]

With this apparatus it was found that a polished quartz plate had a reflecting power of about 0·33 per cent. at $\lambda = 7{\cdot}4\mu$, and at $\lambda = 8{\cdot}5\mu$ the reflecting power was about 75 per cent., equal to that of polished silver for ultra-violet light. On examining the amount of light transmitted it was found that absolute absorption takes place for rays between $\lambda = 8\mu$ and $\lambda = 9\mu$.

Immediately following this paper is one by Rubens and Nichols,[2] dealing with the metallic reflection occurring with quartz and other

[1] See Chapter III., p. 80.

[2] *Ann. der Phys.*, **60**, 418 (1897).

substances. The method of experiment was very similar to that used by Nichols, but the rays from the heat source were made to undergo three or four reflections before entering the spectrometer. A grating was employed which was made by winding silver wire round a frame, and, as the wire was 0·1858 mm. thick, and the grating space 0·3716, it follows that the spectra of even orders were absent. A bolometer was used with fine platinum strips 0·5 mm. broad and 0·001 mm. thick; also a radiometer exactly similar to that used by Nichols in all respects, except that the fluor-spar and mica windows were removed, and one 2·5 mm. thick of silver chloride was substituted. This instrument, however, could not be used for the rays of greatest wave-length owing to their absorption by this window. The name given by Rubens and Nichols to the rays obtained by metallic reflection is "residual rays" (Reststrahlen), and the properties of these rays were investigated for many substances, of which the most important for our present purpose are quartz and fluorite. In the case of the former metallic reflection was found to take place at three points of the spectrum, viz. $\lambda - 8{\cdot}50\mu$, $\lambda = 9{\cdot}02\mu$, and $\lambda = 20{\cdot}75\mu$, of which the first two correspond to those found by Nichols, and the last one is generally known as the residual ray of quartz. In the case of fluorite the residual rays have a wave-length of $\lambda = 24{\cdot}4\mu$, and, after passing through a silver chloride plate, a wave-length of $\lambda = 23{\cdot}7\mu$, showing that the rays of mean wave-length of $\lambda \doteq 24{\cdot}4\mu$ are not homogeneous. Further, the absorption of these rays by various substances, and the indices of refraction of rock-salt and sylvin for these rays were measured, and also their electro-magnetic character was proved. The absorption and refracted indices were examined further, and published in a later communication[1] by Rubens and Trowbridge, and the absorption by Rubens,[2] and by Rubens and Aschkinass.[3] The residual rays of rock-salt and sylvin were investigated by the last two observers[4] with exactly similar apparatus, with the exception that a thermopile was used in place of the bolometer and radiometer which had been previously used. This instrument consisted of twenty elements of iron and the alloy constantan; short wires of these metals were soldered together, and the alternate joints were arranged together so as to form a vertical line about 18 mm. long. This vertical line only was well covered with soot and exposed to the radiations; the resulting potential difference was measured by means of a galvanometer which gave a throw of 1 mm. upon the scale with the current of $1{\cdot}4 \times 10^{-10}$ amperes; and thus the accuracy of the reading of temperature was $1{\cdot}1 \times 10^{-6}$° C. The rays came from an incandescent gas mantle, and were reflected five times from sylvin or rock-salt faces. The wave-lengths of the residual rays were found to be, for rock salt, $\lambda = 51{\cdot}2\mu$, and for sylvin, $\lambda = 61{\cdot}1\mu$.

Later, Rubens and Aschkinass devised a method of separating the long rays by passing through them a quartz prism of very narrow refracting angle; for, though this substance absorbs rays of shorter wave-length, yet it is very reasonably transparent to these rays—a quartz plate

[1] *Ann. der Phys.*, **60**, 724 (1897).
[2] *Ibid.*, **64**, 584 (1898).
[3] *Ibid.*, **64**, 602 (1898).
[4] *Ibid.*, **65**, 241 (1898).

0·5 mm. thick allows 61 per cent. of the residual rays from rock-salt and 77 per cent. of those from sylvin to pass. A diagram of Rubens's apparatus is shown in Fig. 112; A is the source of light, and s_1 is the first slit; the light then falls upon a concave mirror e_1, whence it falls as a parallel beam on to the grating g and the second concave mirror e_2. This mirror focusses the rays upon the second slit s_2, after leaving which they undergo five reflections from the surfaces p_1, p_2, p_3, p_4, and p_5, of the material under investigation. The rays are finally focussed by the mirror H on to the thermopile T. K is a large chest which encloses the apparatus from stray heat waves, and the thermopile is further protected by being placed within an inner chamber.

In Fig. 113 is shown a plot of the results obtained for rock-salt, in which the ordinates are the excursions of the galvanometer needle, and

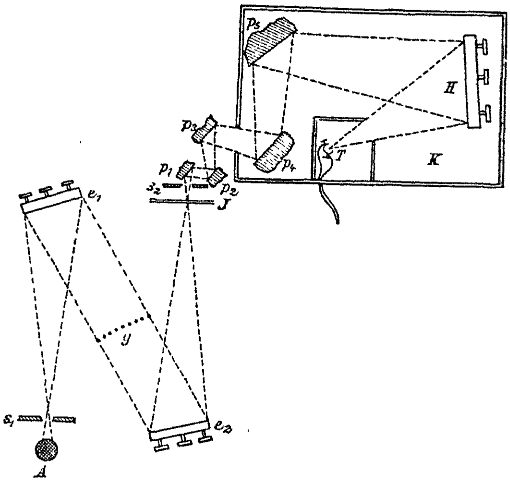


FIG. 112.

abscissæ the deviations produced by the grating. The maximum plotted in the centre, of course, corresponds to the rays transmitted directly through the grating, while the two side maxima are due to the residual rays when diffracted by the grating on each side of the normal. The refractive indices measured by Rubens and his co-workers will be found under the heading of prisms in Chapter III., and therefore will not be given again here.

Rubens and Hollnagel[1] adopted the interference method for the investigation of radiations of long [illegible]. Th[illegible] interferometer they used was similar to that emplc[illegible] for obtaining his "visibility" curves (see Volume II., Chapter I.), the only difference being that very thin quartz plates were used in place of the glass ones used by

[1] *Berl. Ber.* (1910), 26; and *Phil. Mag.*, **19**, 761 (1910).

Michelson, in order to reduce the absorption of the rays to a minimum. In one case a plane parallel pair was used, each being 0·6 mm. thick, and in the other case a wedge-shaped pair tapering from 0·8 to 0·4 mm. thick was used. The pitch of the micrometer screw was 0·5228 mm., and as the drum actuating this screw was divided into 100 parts, a rotation of one division corresponds to a displacement of 5·228μ.

The arrangement of the apparatus was very similar to that already described under Rubens's work, with the addition that the rays from the source pass through the interferometer before they fall on the reflecting surfaces of the substances to be investigated. The source of energy was a Welsbach burner, the rays from which were focussed by a concave

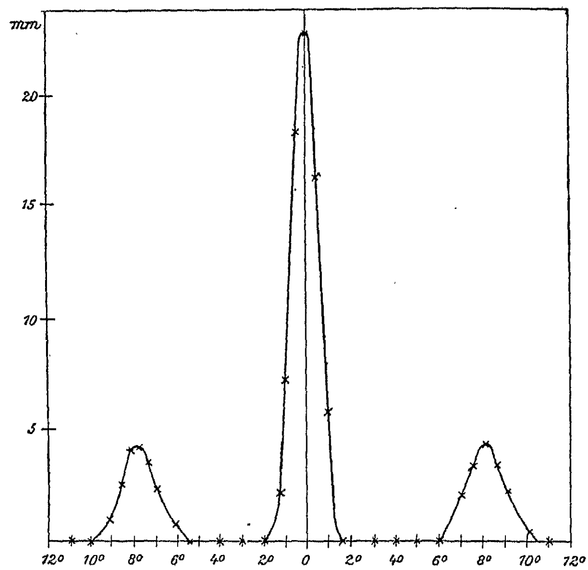


FIG. 113.

mirror on to the air space between the interferometer plates. After emerging from the interferometer the rays were reflected four times from the polished surfaces of either sylvin, potassium bromide, or potassium iodide, and were then focussed by a second concave mirror upon the thermo-junction of a very delicate radiomicrometer. By altering the distance between the interferometer plates, and measuring the energy received by the radiomicrometer, it will be seen that a "visibility" curve can be constructed in which the ordinates represent "intensities of radiation" and the abscissæ the distances between the interferometer plates. The distribution of energy in the radiation from the source was calculated in a very similar way to that used by Michelson in his experiments. The reflecting plates of sylvin were obtained simply enough by cutting a block of this material obtained from Stassfurth. In the

case of the potassium bromide and iodide the following method was employed. A quantity of the salt was melted in a nickel crucible and the molten mass poured into a brass vessel 10 cms. square and 1·5 cms. deep and then allowed to cool. Such blocks were rendered plane by turning in a lathe. No difficulty was experienced in grinding and polishing the potassium bromide, but considerable difficulty was found in dealing with the iodide. In this case good surfaces were ultimately obtained by grinding against one another, until they were dry, two surfaces previously moistened with water. Such surfaces, when carefully ground, were polished with the palm of the hand, using diamantine powder and paraffin oil. It was found that these mirrors preserved their polish for several days. The wave-lengths of the residual rays were as follows:—

	μ	μ	λ_0	*mw*
Rock-salt	53·6	46·9	51·7μ	58·5
Sylvin	62·0	70·3	63·4μ	74·6
Potassium bromide	86·5	75·6	82·3μ	119
Potassium iodide	96·4		96·4μ	166

It will be seen from the above table that potassium iodide only gives one radiation, whilst the other three substances give two. In the third column of the table headed λ_0 are given the means of the wave-lengths, and in the last column the molecular weights of the compounds. It will be seen that the mean wave-length increases more rapidly than the square root of the molecular weight and less rapidly than the molecular weight itself.

A still further improvement in the method of isolating the very long heat waves has been made by Rubens and Wood.[1] The method is based on the selective refraction by quartz lenses, for which material the refractive index for the light and the short heat waves lies between 1·43 and 1·55, whilst for the very long heat waves the refractive index approximates to 2·14, which is the square root of the dielectric constant for slow oscillations. The arrangement of lenses is shown in Fig. 114, which is taken from Rubens and Wood's paper. The two lenses L_1 and L_2 have a diameter of 7·3 cms. and a thickness of 0·8 cm. in the middle and 0·3 cm. at the edge. Their focus for the mean light rays is 27·3 cms. The radiation from a Welsbach burner A passes through a circular aperture 15 mm. in diameter B in a screen made of two large sheets of tin plate, and then through the quartz lens L_1, a second aperture F and the quartz lens L_2, which focusses them on the thermo-couple of the radiomicrometer M. The central zones of the two lenses are covered by circular discs of black paper a_1 and a_2, 25 mm. in diameter. A movable shutter D is used to cut off the radiation at will. The distance of the

[1] *Phil. Mag.*, **21**, 249 (1911).

lenses from the circular aperture is so arranged that a sharp image of the circular source B is focussed upon F only for radiation, for which the refractive index for quartz is 2·14. The path of these very long waves is shown in the diagram by the coarse dotted lines. Owing to the very much smaller indices of refraction for the light waves and short heat waves it is evident that these, after emerging from the lens L, will form a divergent cone shown by the fine dotted lines in the diagram. The central portion of this cone, such as would otherwise fall on the aperture F, is intercepted by the small black screen a_1. As a result of this only the very long heat waves can pass through the aperture F. The second quartz lens L_2 acts in exactly the same way, and still further purifies the radiation.

The great advantage of this method of focal isolation is that large angular apertures can be used, and the radiation is weakened only by reflection and absorption by the two quartz lenses. Its only disadvantage is that all radiations for which the refractive index approxi-

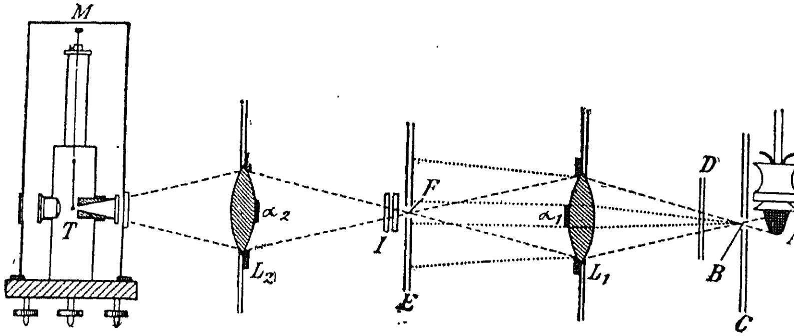


FIG. 114.

mates to 2·14 pass through the apertures. For $\lambda = 63\mu$ the refractive index of quartz is 2·19, decreasing to 2·14 as the limiting value. The very powerful absorption of quartz for rays between 60μ and 80μ prevents the shorter waves from getting through the system. Beyond 80μ the quartz begins to show stronger transparency, 17 per cent. of the residual rays from potassium iodide passing through a quartz plate 18 cms. thick, which is about the amount of quartz present in the path of the rays. The result of this is that the energy curve of the transmitted radiation is very steep on the shorter wave-length side, whilst on the other side it slopes gradually at a rate determined by the energy curve of the light source, which decreases as the fourth power of the wave-length and the increase in transparency of the quartz with the increasing wave-length.

Rubens and Wood describe in their paper the result of some investigations with this apparatus. In order to determine the wave-length of the radiations they made use of the quartz interferometer of Rubens and Hollnagel as described above. The only difference in the instru-

ment was that the quartz plates were rather thicker, two pairs being used, one 1·2 mm. and the other 7·3 mm. thick. In Fig. 115 is shown one of the "visibility" curves obtained, in which the ordinates represent the radiomicrometer deflections in millimetres and the abscissæ represent the thicknesses of the air film expressed in sodium wave-lengths. This curve shows a minimum at 46λ and a maximum at $85\lambda_D$ and a second minimum at $122\lambda_D$. The mean wave-length of the radiation complex is found from this curve to be $108{\cdot}2\mu$, 100μ, and $96{\cdot}3\mu$, according to whether the first minimum or the maximum or the second minimum is used in the calculation. The explanation of this difference lies, of course, in the unsymmetrical character of the energy curve. The first minimum gives the value of the wave-length corresponding to the

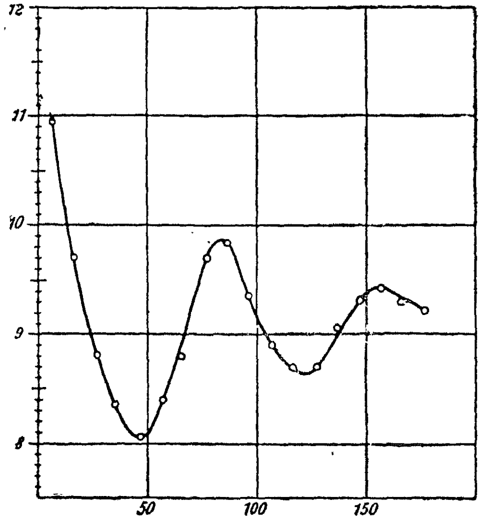


FIG. 115.

centre of gravity of the wave-curve, while the following maximum and minimum approach more and more nearly to the wave-length of the maximum in the energy curve. By the process of trial by error the authors constructed an energy curve which would give the same "visibility" as that shown in Fig. 115. This curve shows very conclusively that the maximum radiation is about 96μ, and that there are present in the radiation from a Welsbach burner rays certainly as long as 150μ, and probably as long as 200μ.

It has been shown possible to combine the method of residual rays with the method of focal isolation as described above, for Rubens [1] has isolated the residual rays of calcite by passing through the quartz lens apparatus the rays successively reflected from two calcite mirrors. The

[1] *Verh. der Deutsch. Phys. Gesell.*, **13**, 102 (1911).

result was a pure and bright pencil of residual rays. It was evident, on a comparison between the radiomicrometer deflection obtained with the apparatus with and without the calcite mirrors, that a considerable selective weakening was sustained by the radiation on reflection at the two calcite surfaces, and also that the reflection made the radiation more homogeneous. The wave-lengths of the residual rays were determined by means of the interferometer, as already described, and from an analysis of the "visibility curve" it is found that they consist of a strong band at 93μ and a weaker band at 116·1μ. The mean wave-length, *i.e.* the optical centre of gravity, is calculated to be 98·7μ.

The application of the focal isolation method has enabled Rubens and von Baeyer[1] to discover the existence of waves of exceedingly long wave-length in the emission spectrum of quartz mercury lamps. They investigated the radiation from a large number of sources, including sparks between various metal electrodes and the arc between carbon electrodes. It was at once found on trying with a quartz mercury lamp that there is present a very strong long-waved radiation, and it was soon discovered that this radiation must possess an essentially different composition from that of the Welsbach mantle, the mean wave-length of which is 108μ. For instance, a layer of quartz 14·6 mm. thick transmits 46·6 per cent. of the mercury lamp radiation and only 20 per cent. of the Welsbach mantle radiation. A number of experiments were carried out to test the transmitting power of various substances for these rays and for the rays from the Welsbach mantle. About seventeen different substances were experimented with, and in every single case the percentage transmission for the mercury lamp radiation was greater than for the Welsbach mantle radiation. Further, it was found that the percentage transmission was increased very materially if these radiations were previously passed through a 2 mm. layer of fused silica. It is evident, therefore, that the fused silica acts as a filter and cuts off some of the shorter wave-length radiation. Therefore, the percentage of transmission given by the same set of substances with the Welsbach radiation is very much smaller. Further experiments showed that the most effective ray filter is black cardboard, and the authors finally substituted for the silica a filter of black cardboard 0·38 mm. thick. In order to determine the average wave-length of these radiations attempts were made to measure them by the quartz interferometer, as already described. The interferometer curves obtained with the quartz mercury lamp without any filter showed a very irregular character. Nevertheless, it was evident that the main element of the radiation was about the same mean wave-length as that already dealt with from the Welsbach mantle. As soon as a 15 mm. layer of quartz was inserted a very considerable difference in the curve was noticed, for the first minimum which previously was observed at a thickness of the air film of about 26μ now did not appear until the air layer was 42μ thick. If the thickness of the quartz filter was increased to 42 mm. the first minimum was not observed until the air layer of the interferometer was 68μ thick.

[1] *Phil. Mag.*, 21, 689 (1911).

At the same time the interferometer curve became more regular, and the faintly marked maximum began to make its appearance. With a filter of black cardboard 0·4 mm. thick the periodic nature of the curve becomes more distinct. Here the minimum lies at a thickness of 78·4μ, and a strong maximum at 156·9μ, but even in this case an accurate determination is still very difficult. It is evident, as is previously deduced from experiments on transmission, that the radiation after filtration through black cardboard contains a greater amount of the long wave radiation. It is still doubtful whether the long wave radiation consist of rays of different wave-length such as would be expected if they arose from the luminiferous radiation of mercury vapour, or whether it is simply a continuous thermal radiation. It is, however, safe to deduce from the observations that a large portion of this radiation possesses a mean wave-length of 314μ, or very nearly one-third of a millimetre. It may be added that Rubens and von Baeyer satisfied themselves that the radiation in question has its origin in the mercury vapour itself and not in the hot quartz walls of the lamp.

More recently the selective radiation from the quartz mercury lamp has been investigated by Rubens.[1] Three gratings, 8 × 8 cm., were used made of copper wire of thicknesses 1·004 mm., 0·483 mm., and 0·196 mm., the grating spaces being 2·0027 mm., 0·9991 mm., and 0·3997 mm., respectively. Two series of measurements were made which extended to as far as the wave-length $\lambda = 400\mu$ and the wave-lengths of the emission maxima were found to be as follows:—

First series.	Second series.
72·2μ	69·9μ
149·9μ	151·2μ
209·9μ	210·9μ
324·8μ	324·8μ

The last maximum is the longest wave-length yet detected in a selective emission spectrum.

Since the time Rubens first discovered the existence of the residual rays and measured the wave-lengths of those arising from calcite, fluorite, sylvin and quartz, the residual rays from many other substances have been observed by various experimenters. In the following table are given the values obtained by Porter :—[2]

Marble	6·77μ	Ammonium Chloride	3·44μ
Potassium Bichromate	10·31μ	Potassium Sulphate	8·42μ
Copper Sulphate	2·30μ	Potassium Bisulphite	8·21μ
Tartaric Acid	4·72μ	Potassium Ferrocyanide	4·84μ

Nichols and Day[3] obtain the following values :—

Rock Salt	52·3μ	Witherite	46·0μ
Ammonium Chloride	51·4μ	Strontianite	43·2μ

[1] *Berl. Ber.*, 1921, 8. [2] *Astrophys. Journ.*, **22**, 229 (1905).
[3] *Phys. Rev.*, **27**, 225 (1908).

Nichols and Day pointed out how the wave-length of the residual rays follow the atomic weight of the metallic radicle in the salt; for example, in the chlorides of sodium, potassium and ammonium, in which the atomic weight relations are 39, 23 and 18, the wave-lengths of the residual rays are in the same order, $61 \cdot 1\mu$, $53 \cdot 3\mu$ and $51 \cdot 4\mu$. Similarly, in the case of barium and strontium, of which the atomic weights are 137 and 88, the wave-lengths of the residual rays are 46μ and $43 \cdot 2\mu$

It has already been pointed out that the residual rays are due to what is known as metallic reflection of those rays for which the substance in question possesses powerful absorption. It is evident that if the phenomenon is really one of metallic reflection that the rays reflected must be elliptically polarised. The existence of this elliptical polarisation of the infra-red rays was proved by Pfund,[1] who used a polariser and analyser made of selenium plates set at the polarising angle. He found that the reflecting power of selenium between 2μ and 13μ is extraordinarily constant, and the first question taken up was whether these reflected infra-red rays are polarised by the selenium. This was proved by the ordinary method of adjusting the mirrors till maximum polarisation is obtained and then crossing them. The radiometer readings now showed a ratio of 1000 : 1, showing that the radiation is plane-polarised to a very high degree. Deflections of the radiometer were observed as far as 13μ, so that it is clear that the infra-red rays are capable of being polarised as far as this wave-length, which is as far as the apparatus allows.

In order to determine whether a non-metallic substance such as calcite in its region of metallic reflection behaves as a metal towards plane-polarised light, a polished plate of calcite was set up between the analyser and the polariser so as to reflect the plane-polarised light reflected from the first selenium mirror. The readings of the radiometer were then observed corresponding to the two positions of the analyser giving maximum and minimum energy. When $\lambda = 4\mu$, where the calcite only reflects vitreously, these readings were in the ratio 500 : 0, but when $\lambda = 6 \cdot 7\mu$ where the calcite reflects metallically, the radiometer readings were in the ratio 90 : 50. This shows conclusively that calcite transforms plane-polarised waves into elliptically-polarised waves within the region of metallic reflection.

The following residual rays have been measured by Rubens[2] during recent years :—

Silver chloride	$81 \cdot 5\mu$
Lead chloride	$91 \cdot 0\mu$
Thallium chloride	$91 \cdot 6\mu$
Mercurous chloride	$98 \cdot 8\mu$
Silver bromide	$112 \cdot 7\mu$
Thallium bromide	$117 \cdot 0\mu$
Thallium iodide	$151 \cdot 8\mu$

[1] *Astrophys Journ.*, 24, 19 (1906).
[2] Rubens, *Berl. Ber.*, 1913, 513; Rubens and von Wartenberg, *ibid.*, 1914, 169.

Amongst Rubens' last work there may be noted an important in-
estigation on the reflection and transmission of selective rays of
ɔng wave-length by various natural crystals.[1] These selective rays
ere passed through different thicknesses of quartz, etc., in order to
btain homogeneous radiation in each case. The wave-lengths were as
ɔllows :—

Residual Rays from	*Transmission Screens.*	*Wave-lengths.*
Fluorite	6 mm. of sylvin	22μ
Fluorite and calcite	3 mm. of potassium bromide . . .	27μ
Fluorite	0·4 mm. of quartz	33μ
Aragonite	0·4 mm. of quartz	39μ
Rock-salt	0·8 mm. of quartz	52μ
Sylvin	0·8 mm. of quartz	63μ
Potassium bromide	0·8 mm. of quartz	83μ
Potassium iodide	0·8 mm. of quartz	94μ
Thallium bromide	0·8 mm. of quartz	117μ
Auer-burner	These were isolated by quartz . .	110μ
Quartz mercury lamp	lens method	324μ

'he radiation in each case was plane-polarised to the extent of 68·5 per
ent. by reflection from a selenium mirror, and the natural crystals were
efinitely oriented with respect to the plane of polarisation.

Substance.	Direction of oscillation.	Short wave bands in μ.	Long wave bands in μ.
uartz	$\parallel$	8·50, 8·70, 8·90, 9·05, 12·87	19·7, 27·5
	$\perp$	8·50, 8·90, 9·05, 12·52	21·0, 26·0
alcite	$\parallel$	11·30	28·0, 94
	$\perp$	6·46, 6·96, 14·17	30·3, 94
patite	$\parallel$	—	32, (135)
	$\perp$	—	30, 45, (140)
olomite	$\parallel$	11·43	27·5, 68
	$\perp$	6·90	29, 74
ed tourmaline . . .	$\parallel$	9·0, 12·75, 14·2	43, 97
	$\perp$	7·70, 10·1	43, 82
arytes	a	8·93	62, 97
	b	—	61, (120)
	c	8·30	51, (130)
ɔlestine	a	8·84	48, 85
	b	9·05	58·5, (135)
	c	8·35	45·5, 84
nglesite	a	—	63, (98)
	b	—	67, 97
	c	—	
nhydrite	a	—	35, (45-50)
	b	—	35, (45-50)
	c	—	
·agonite	a	11·55	36·5, (50), 85
	b	6·46, 6·70, 14·17	36·5, (50), 100
	c	6·65, 14·06	34, (50), 88
ɔrussite	a	12·00	64, 94
	b	7·04	64
	c	7·28	64

[1] Liebisch and Rubens, *Berl. Ber.*, 1919, 198 and 876.

From the curves obtained it was possible to determine the position of the reflection maxima, that is to say, the absorption bands in each case. The results are given in the above table.

A very remarkable fact is evidenced by the above results, namely that the absorption bands exhibited differ according to the orientation of the crystal to the plane of polarisation of the incident energy in the long wave region.

Very valuable work has also been carried out by Paschen, this being of three kinds. In the first place, he investigated the normal emission spectrum of an absolutely black body at different temperatures. In the second place, he determined with great accuracy the dispersion curves of fluorite and rock-salt, and lastly he has published several important papers on the emission spectra of elements in the short wave region of the infra-red.

In the first-named investigations Paschen employed both a radio-micrometer and a bolometer for the measurement of the intensity of the radiation. The first instrument is a modified form of that invented and used by Boys [1] for the measurement of the heat of the moon and stars, etc. This instrument, as modified by Paschen,[2] may be described as follows: two alloys are prepared, one containing ten parts of bismuth and one part of antimony, and the other equal parts of cadmium and antimony; both of these alloys are cast into very small slabs, 0·3 mm. thick, 0·5 mm. broad, and 4 to 5 mm. long. One of each kind of these strips is soldered to a strip of silver 0·5 mm. broad, 0·03 mm. thick, and several mm. long; this operation is carried out by heating the silver and gently pressing the alloy against it, when a good joint will be obtained. The general arrangement is shown in Fig. 116, where *a* and *b* are the little slabs of the two alloys which are soldered to the silver strip *c*. To the upper ends of these slabs and on the inner sides, the two ends *d*, *e* of a thin silver wire are soldered; this wire is bent round to a hoop as is shown at *c* in Fig. 117. A very thin glass rod, G, is fastened to the silver wire, and carries a mirror, S, the whole being suspended by a quartz fibre, Q. It is, of course, necessary that the whole hang vertically and swing on its central vertical line. The thermocouple is suspended in the centre of a thick iron block, E, as shown in Fig. 118,[3] and the iron block E in its turn is set inside a copper block; a hole is bored, as shown, to admit the radiations; the silver hoop *a* hangs in a copper tube, R, which also has a window for the illumination of the mirror *c*.

The poles N, S of a magnet are brought up against the opposite sides of the copper block, and the whole thermopile is made as small as possible, so that it all lies in an equal magnetic field. The portion of the silver strip exposed to the radiations is well covered with soot, in order to absorb them with greater ease. The apparatus thus consists of a very small thermopile, which is formed of a triple junction instead of the usual couple. By the construction it will be seen that only the

[1] *Phil. Trans.*, **180**, A, 159 (1889). [2] *Ann. der Phys.*, **48**, 272 (1893).
[3] Boys, *Phil. Trans.*, **180**, A, 183 (1889).

ower junction can get heated, and by this a small current will be sent ound the silver wire, which will cause the rotation of the instrument in ne magnetic field. Generally, as Paschen says, the first test of an instruent will show that it is very unsensitive. This is owing to the para r diamagnetic properties of the materials used. For every instrument nere will be found a particular strength of magnetic field for which the reatest sensitiveness is obtained. Those which give the smallest os-

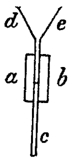


FIG. 116.

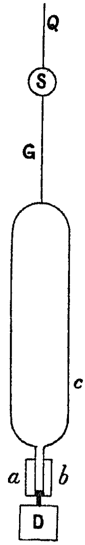


FIG. 117.

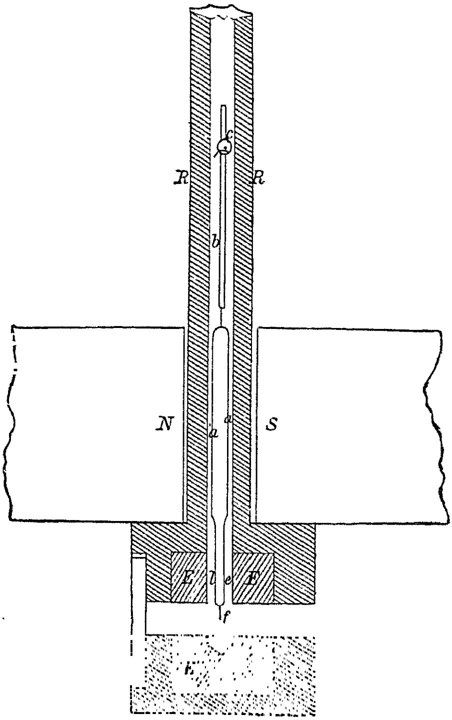


FIG. 118.

illation period in strong fields are the best. The alloys may be obined sufficiently free from iron by repeatedly melting them, and the lver by electrolytic deposition. Less diamagnetic circuits are obtained y using for the hoop silver wire drawn through an iron wire-drawing late. Paschen never succeeded in making an instrument completely ndifferent to a magnet. He made two instruments, which were equally ensitive in the same field, and gave with a candle at 6 metres distance a novement of the spot of light over sixty to seventy divisions with an scillation period of forty seconds.

Paschen has also employed a bolometer, in which he used the platinum-silver foil according to Lummer and Kurlbaum's method.[1] Three strips, 0·001 mm. thick (platinum, 0·0005 mm. thick), 0·5 mm. broad, and 15 mm. long, were stretched as close to one another as possible, and formed one arm. Only those portions exposed to the radiations were freed from silver, and then they were sooted. The compensation resistance was adjustable by means of mercury contacts actuated by micrometer screws.

The galvanometer[2] used in connection with the bolometer had a degree of sensitiveness such that a movement of the spot of light 1 mm. upon the scale at 2·7 metres distance corresponded to a current of $1·6 \times 10^{-11}$ amperes. The bolometer could carry a current of 0·06 ampere without disturbing the galvanometer needle, but only 0·038 to 0·04 ampere was generally used, and the delicacy was then found to be such that 1 mm. throw on the galvanometer scale was produced by a change of temperature of $\frac{1}{1000000}$° C.

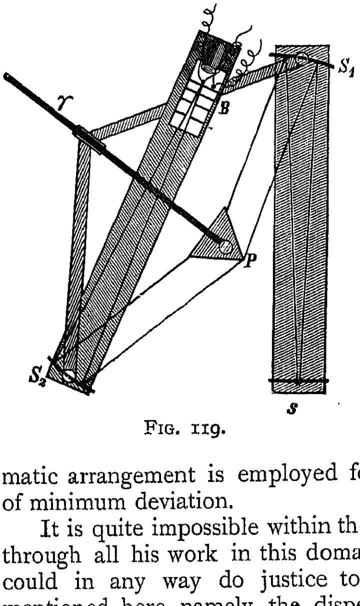


FIG. 119.

The arrangement of Paschen's apparatus is shown in Fig. 119; it may be pointed out that he was the first to substitute concave mirrors for rock-salt lenses, thereby doing away with, amongst other objections, chromatic aberration. The rays enter the slit *s* and fall on to the concave mirror S_1, by which they are directed as a parallel beam through the fluorite prism P on to the concave mirror S_2, which focusses them on to the bolometer at B. As will be seen, an automatic arrangement is employed for keeping the prism in the position of minimum deviation.

It is quite impossible within the scope of this book to follow Paschen through all his work in this domain, and give an account of it which could in any way do justice to it. One section of it only can be mentioned here, namely, the dispersion of fluorite.[3] In this investigation it was necessary to employ a linear bolometer, and not a surface instrument such as was described above; the three platinum strips, used in the latter case, were replaced by a single strip of platinum, sooted on one side, 7 mm. long, 0·25 broad, and 0·0005 mm. thick, with a resistance of 8 ohms. This instrument had about the same sensitiveness as the former instrument. One of Rowland's gratings was used, which had been specially ruled for Langley. This grating had a ruled surface of

[1] See below, p. 247.
[2] *Zeitschr. für Instrumentenk*, 13, 17 (1893).
[3] *Ann. der Phys.*, 53, 301 (1894).

132 mm., with 142·1 lines to the millimetre, and a focus of 1·753 metres. The results of these measurements are given in Chapter III., p. 80.

Paschen[1] has also carried out very valuable work on the selective emission spectra of elements in the infra-red region. This work is especially important in connection with the problem of the series of lines in spectra, and the results obtained by him will be given in Volume II., Chapter XI. It is only necessary here to give a brief mention of the apparatus used. Paschen employed in these researches a bolometer or a thermopile. The latter instrument was of the Rubens pattern and the junctions were made of iron and constantin. His observations extended as far as the wave-length of $5·4\mu$. This particular branch of investigation has been continued by other observers, but inasmuch as no essentially new methods have been developed this brief reference is all that is necessary in this place, since the actual results will be dealt with in the next volume.

There is another branch of investigation which has been carried out, namely, the measurement of the selective absorption of energy in the infra-red by various substances. A portion of this work has already been mentioned under residual rays, which of course indicate the existence of a power of selective absorption of those rays by the substance in question. The residual ray method is in general only applicable to solids, since a polished plane surface is required. On the other hand, a considerable amount of work has been done on the selective absorption exhibited by liquids and gases, and there is no question but that the results are of far-reaching importance. One of the first to enter this field was Coblentz, who carried out an extended investigation into the infra-red reflection and transmission spectra of a great number of minerals, with the view of determining, if possible, the relation between their constitution and the absorption which they exert.[2] The apparatus consisted of a mirror spectrometer, a rock-salt prism, and a Nichol's radiometer. The rock-salt prism had faces 9·9 cms. square, and the radiometer required about twenty seconds to reach its maximum deflection. The source of energy employed was a 110-volt Nernst lamp fed from an 80-volt storage battery. The radiometer only differed from the one described above by being covered with a heavy piece of brass tubing, within which was a layer of coarse felt. The sensitiveness of the instrument was about 10 cms. deflection per square millimetre of

[1] The following is a list of Paschen's papers upon his work in the infra-red: *Bolometrische Untersuchungen im* [illegible] *der Phys.*, **48**, 272 (1893); *Die Gesammtemission glühenden Plati*[illegible] **49**, 50 (1893); *Die Emission der Gase, Ann. der Phys.*, **50**, 409 (1893); **51**, 1 (1894); **52**, 209 (1894); *Die Dispersion des Fluorits im Ultraroth, Ann. der Phys.*, **55**, 301 and 812 (1894); **56**, 762 (1895); **41**, 670 (1913); *Die Dispersion des Steinsalzes im Ultraroth, Ann. der Phys.*, **55**, 337 (1894): *Gesetzmässigkeiten in der Spectren festen Körper, Ann. der Phys.*, **58**, 455 (1896); **60**, 662 (1897); *Die Vertheilung der Energie im Spectrum des schwarzen Körpers, Berl. Ber.*, 1899, 405 and 959; *Ann der Phys.*, **38**, 30 (1912); *Emission Spectra of Elements in the Infra-red, Ann. der Phys.*, **27**, 537 (1908); **29**, 625 (1909); **33**, 717 (1910); **36**, 191 (1911).

[2] *Investigations of Infra-Red Spectra*, Publications of the Carnegie Institution, Washington, 1905 and 1906.

exposed surface with scale and candle at one metre distance. The accuracy, judging by repeated series of measurements at various times, was about 0·02μ.

The absorption and reflection spectra of at least 125 elements and substances have been examined, many of them to as far as 15μ. The principal object of this investigation was to gain information with regard to the molecular structure of minerals containing oxygen and hydrogen. A detailed account of Coblentz's results would be out of place here, but there is no question of any doubt that very valuable knowledge has been gained of the vexed problem of the constitution of minerals.

The organic chemist by his own particular methods is able to study the constitution of the compounds with which he has to deal, but the mineralogist is unable to do this. The relation between absorption and constitution in the case of organic compounds has carried us far towards a comprehension of what is the real meaning of chemical reactivity and chemical combination. Owing to our entire ignorance of anything more than the empirical formulæ and crystalline structure of minerals, it is not surprising that the tentative rules for classifying minerals break down in certain cases. It is therefore to such investigations as that of Coblentz that the mineralogist must look for a solution of his problems.

The investigation of infra-red absorption spectra received a great stimulus in 1912 when Bjerrum enunciated his conception of molecular rotation. The fundamental basis of this theory is that in addition to the characteristic frequencies in the infra-red established by its chemical nature a molecule will also possess a frequency in the long wave infra-red established by its rotation. Bjerrum stated that the result of this will be that the characteristic frequencies in the short wave region will not evidence themselves as single absorption lines but as groups of three frequencies, $F + R$, F, $F - R$, where F is the frequency in the short wave region and R is the rotational frequency. When as in actual practice a number of molecules are present there will be found at F an absorption band containing the frequencies $F + nR$, F, and $F - nR$, where $n = 1, 2, 3$, etc. Further, there will be found in the long wave region a series of absorption lines with the frequencies nR. From investigations made by Miss von Bahr in Rubens's laboratory strong support was found for Bjerrum's theory and since then further important results have been obtained on the structure of absorption bands.

In addition to this Coblentz has carried out an investigation of the absorption spectra of a large number of organic compounds. Although he was unable to find a complete explanation of the absorption curves which he obtained, he established two facts of very great significance. He showed, in the first place, that definite absorption frequencies can be attributed to specific atomic groups in the molecules of the compounds he examined. Amongst these were the CH_3, C_6H_5, NO_2, NH_2, and OH groups. In the second place, he established the existence of harmonic relations between the centres of some of the absorption bands exhibited by certain compounds.

These results found by Coblentz, together with the observations based on the Bjerrum theory, are of very great importance, as will be shown in the discussion of absorption spectra (Vol. II., Chapters VI. and VII.). Reference is made to them here with the view of indicating that a new field of work has been opened up by these investigations and that this line of research is in all probability one of the most promising fields in terrestrial spectroscopy.

The methods employed in the investigations quoted above did not differ materially from those adopted in the older work. The chief point to be noticed is the steady advance in technique with the result that the fine line structure of infra-red absorption bands can now be observed with considerable precision. This has been secured, not so much by modification of the methods, as by improvements in the resolving power of the dispersing apparatus and in the delicacy of the recording instrument.

Mention was made in Chapter VI. of Wood's method of ruling reflecting gratings for use in investigations of the infra-red.[1] He gave the name of echelette gratings to these instruments and a short note may be given on some of the results obtained by their use. Trowbridge and Wood[2] found that on applying this grating to the study of infra-red region a higher resolving power is obtained than has ever yet been applied to the infra-red region. These investigators find that the residual rays of quartz show two maxima of which the longer wave-length one is considerably higher than the shorter wave-length one with a shallow minimum between them. The echelette grating shows that the maxima are nearly the same height, and the minimum between them is very much deeper than was previously supposed, its intensity being only one-third that of the maxima. The wave-lengths of the two maxima are found to be $8{\cdot}41\mu$ and $8{\cdot}30\mu$. Similarly with regard to the radiation from the carbon dioxide in a bunsen burner, the echelette grating resolves a strong band at $4{\cdot}3\mu$ into two, the wave-lengths of which are $4{\cdot}32\mu$ and $4{\cdot}43\mu$.

Recently the echelette grating has been used in connection with the most sensitive recording apparatus for the study of the absorption exerted by gases. In one case echelette gratings, ruled with 3000, 1000, and 500 lines to the inch on aluminium surfaces, were employed in conjunction with a narrow angle (38°) rock-salt prism, this being used to eliminate the overlapping of the different spectral orders.[3] A silver-bismuth thermopile was used in conjunction with a Paschen galvanometer. With this apparatus the absorption and emission bands of carbon dioxide were observed and their wave-lengths measured.

In the second case an echelette grating was used for the examination of the structure of the absorption band of hydrogen chloride at $3{\cdot}4\mu$.[4] This grating had 2800 lines to the inch, and threw most of the light into the first order in the region $3{\cdot}5\mu$. With this apparatus the

[1] *Phil. Mag.*, **20**, 770 and 886 (1910). [2] *Ibid.*, **20**, 898 (1910).
[3] Barker, *Astrophys. Journ.*, **55**, 391 (1922).
[4] Colby, Meyer, and Bronk, *ibid.*, **57**, 7 (1923).

fine absorption lines forming the structure of this band were readily observed, and their wave-lengths determined with considerable accuracy.

Several very important papers have been published which deal with the construction and relative merits of the four recording instruments—the bolometer, the radiometer, the radiomicrometer, and the thermopile. These may be referred to here, as perhaps they may prove of use to any who wish to undertake work in the infra-red region.

In the first place, certain considerations respecting the construction and use of bolometers have been given by Lummer and Kurlbaum.[1] As a bolometric measurement is nothing more or less than the measurement of a resistance change with a Wheatstone's bridge, therefore the general rule of a Wheatstone's bridge here holds good, namely, that the best relation between the resistances is obtained when the four arms (if four are used) and the galvanometer have the same resistance. In order to obtain the best conditions for a bolometer the following quantities should be made as large as possible :—

1. The chief current through the instrument.
2. The temperature coefficient of the metal strip.
3. The portion of the bolometer resistance exposed to the radiations.
4. The resistance of the instrument.
5. The absorption coefficient of the exposed surface.
6. The irradiated surface.

On the other hand, the following should be as small as possible :—

7. The emission coefficient of the surface exposed.
8. The heat capacity ; in order to ensure this, the thickness of the metal strip should be as small as possible.

In practice, unless precautions are taken to the contrary, it will be found that troublesome movements of the galvanometer needle take place, either in the shape of a steady motion in one direction or of unsteady oscillations. The first of these motions is due to the heating of the bolometer filament by the current flowing through it, whilst the second is due to air currents within the instrument, caused by the heating of the filaments. Concerning the first trouble—namely, the steady motion of the spot of light, which often lasts a quarter of an hour after the current has been started—it is clear that, if all four arms of the bolometer had exactly the same resistance, cross-section, surface, etc., then no change in the spot of light would be obtained, as the changes would be the same in all ; this will be also true, of course, if there be only two arms instead of the four.

We have thus another condition for good working—

9. That the resistance of the bolometer arms must be equal.

10. To meet the second trouble—the irregular oscillations of the spot of light—it is necessary to arrange that the air currents be as regularly distributed as possible. This is a tenth condition for efficiency. As the air currents arise from the heat produced by the current, and as the heat depends upon the current density and the resistance, one might

[1] *Ann. der Phys.*, 45, 204 (1892).

suppose it possible to choose such a resistance that the air currents would be reduced to a minimum; but Lummer and Kurlbaum show that changing the specific resistance and the thickness of the filaments has no effect upon the air currents, as $\frac{c}{\sqrt{R}}$ is a constant where c is the current and R the resistance.

By changing the length of the filament, so that the resistance is n times as great, the throw of the galvanometer mirror is $\sqrt{n}$ times as great. If n filaments are used in parallel or one filament n times as broad, and the current n times as great, this being necessary for equal galvanometer throw, then the same relation is also true, that the throw is proportional to $\sqrt{n}$. In the first case we have a weaker current flowing through a high resistance, and in the second a stronger current through a low resistance. From a practical point of view the first condition is far more convenient, and thus we have another condition for efficiency—

11. That the bolometer consist of a very long and narrow filament.

Lummer and Kurlbaum describe the method of construction of a surface bolometer—that is to say, an instrument for measuring the total radiation from a body; as in the case of a linear bolometer the details are very similar, they may be quoted here at length. The chief difficulty lies, as can readily be imagined, in the preparation of the filament, so that all four arms of the bolometer can be exactly the same in every way as prescribed by condition 9 above. None of the commercially prepared wires are anything like sufficiently accurate, nor is gold leaf, tin foil, or the like of any use. The difficulty of preparing a good filament is perhaps evidenced best by the fact that Julius[1] made use of the nickel plating of his teapot, which he dissolved off with acid. A suitable filament can, however, be prepared in the following way. A piece of platinum foil is welded together with a piece of silver foil about ten times as thick, and the whole rolled out. It is necessary, of course, continually to soften the metal during the process by heating to redness in a charcoal fire, and then plunging into cold water. When the double foil has become very thin, it may be enclosed between two pieces of copper foil, and the whole again rolled. The thickness of the platinum can at any moment be estimated by noting its area. The platinum-silver foil can easily be separated from the copper pieces as long as its thickness is greater than 0·0005 mm. With thinner pieces the silver becomes so pressed into the copper that they cannot be separated. When a sufficiently thin piece of foil has been prepared it is mounted upon a glass plate with Canada balsam, and cut to the required size by means of a dividing engine. For the surface bolometer described by Lummer and Kurlbaum, it is cut into the shape shown in Fig. 120, with twelve parallel strips 32 × 1 mm. and 1·5 mm. apart. It is then dissolved off with chloroform, and mounted upon a slate frame with a solution of colophony in ether, which allows the strip to be accurately

[1] *Arch. Néer.*, **22**, 310 (1888).

adjusted, as it dries very slowly. The appearance when mounted is shown in Fig. 121.

The two ends *a* and *b* are soldered to two pieces of copper foil; these joints and the ends of the filament *m* and *m'* are covered with lacquer. The appearance of the mounted filament from the back is shown in Fig. 122. The whole frame is then placed in dilute nitric acid to dissolve off the silver from the platinum; very great care must be taken not to break the filament in doing so. Special precautions are necessary when washing with water after treatment with acid, as otherwise the surface tension between the acid and water will inevitably break the filament. Paschen, in the description of his linear bolometer, gives a method of doing this. A narrow glass tube sealed at one end is filled with dilute nitric acid so full that a convex meniscus of acid stands above the level of the end of the tube. With this meniscus the etching is done, and then similar menisci of weaker and weaker acid are used, until water is finally employed. The filament is then allowed to dry.

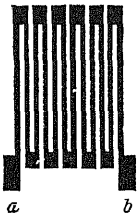


FIG. 120.

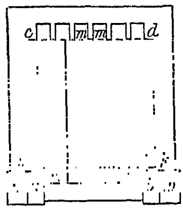


FIG. 121.

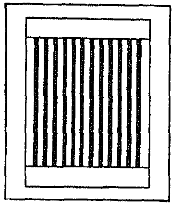


FIG. 122.

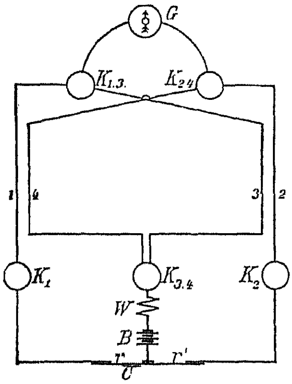


FIG. 123.

The next point is the covering with soot. Lummer and Kurlbaum recommended a small paraffin lamp, *e.g.* a wick placed in a 4-mm. brass tube. A chimney is put round this and on the top is a copper disc about 12 cms. in diameter with a 4-mm. hole in the centre. The bolometer filament is moved about in the soot coming through this hole until it is well covered; only one side of the filament is sooted, the other being protected during the process by a metal plate.

In the four-arm bolometer four such filaments are prepared, all of exactly the same size; the method of connecting them together is shown [illegible] in Fig. 123.

[illegible] the bolometer are placed at 1, 2, 3, 4; G is the galvanometer, and K_1, K_2, etc., are simply plug keys, the numbers signifying the arms they connect together; B is the battery, W a regulating resistance, and *r*, *r'* two mercury contacts. Either 1 and 4 or 2 and 3 are

ɜxposed to the radiation; each arm consists of a filament prepared as lescribed above, and the two together are mounted one behind the ɔther, so that one set of strips is visible between the other set. This :an easily be managed, as the strips are 1 mm. wide, while the distances ɔetween them are 1·4 mm.

One instrument prepared according to these directions gave, with an lectric lamp of 3 candle-power placed at 1 metre distance, a throw of 14·8 mm. As regards the galvanometer, needless to say, a very sensiive instrument must be employed. Paschen describes the making of ne, on the model of Thomson's astatic instrument, to which, however, eference can only be made.[1] The degree of sensitiveness of this instruıent was about $3{\cdot}3 \times 10^{-12}$ amp.

It has been pointed out by Warburg, Leithäuser and Johansen[2] that onsiderable advantage is gained by mounting the bolometer in vacuo. 'hey give a theoretical investigation of the loss of heat by conduction nd radiation, and they find both theoretically and experimentally that reat advantage is gained in the vacuum instrument as regards sensitivity, specially when the bolometer strip is narrow.

An interesting investigation on the sensitivity of the thermopile for ıeasuring radiation has been carried out by Johansen,[3] who gives a ıeoretical discussion of the best conditions obtainable in the use of this ıstrument. He found that a very great improvement is gained by ıounting the instrument in vacuo, and he showed that the loss of heat ue to conduction through the wires of the thermo-junction must be qual to the heat loss due to radiation from the junction, and also that ıe radii of the thermocouple wires must be so chosen that the ratio of ıe heat conductivity to the electrical resistance in each is the same. ɔhansen tested vacuum thermopiles constructed on these principles and und that the sensitivity is equal to the product of the square root of the ırface exposed into a constant. He showed in the case of an instruent used by Rubens that if the value of this constant be put equal to then the value for the vacuum iron-constantan thermopile is 4·5, and r iron-bismuth about 9·5. This means that the sensitivities of these ʋo instruments are 4·5 and 9·5 times that of the Rubens thermopile.

It must, of course, be remembered that the use of a vacuum boloeter or thermopile restricts the use of the instrument to the regions here the window of the exhausted vessel is transparent to the radiations. his objection applies with equal force to the radiometer. It follows at neither of these instruments can be used to investigate the whole of e infra-red, since whatever material be used for the window it will exbit at least one broad infra-red absorption band. This strengthens the se for the general use of the thermopile in air and, as will be seen low, the sensitivity of this instrument has still further been increased.

A very interesting investigation was carried out by Coblentz[4] on the

[1] *Zeitschr. für Instrumentenk*, **13**, 13 (1893).
[2] *Ann. der Phys.*, 24, 25 (1907). [3] *Ibid.*, 33, 517 (1910).
[4] *Bureau of Standards, Bulletin*, 4, 391 (1908).

relative values of the four instruments, bolometer, radiometer, radiomicrometer, and thermopile. He concluded that although the radiomicrometer, such as used by Paschen, may be much improved by placing it in a vacuum it is not nearly so sensitive as the most modern forms of the other three instruments. On the other hand, the design of the radiomicrometer has been considerably improved since Coblentz carried out his first investigations, and he discusses the whole question anew in a second paper.[1] In this paper Coblentz states that in work requiring the highest attainable precision with a great deal of routine observation, extending over a long period, he adopted the vacuum bolometer on account of its quickness in action and on account of the wide range of variation and ease of testing its sensitivity. The instrument, however, is very elaborate and requires very careful handling. In many researches where the actual time consumed in observation is a matter of only a few weeks a radiomicrometer or thermopile would be sufficiently accurate and would require less attention.

The improvement in the radiomicrometer referred to above consists in the employment of a compensating thermo-junction, a device due to Pfund.[2] Two thermo-junctions are used, which compensate one another so that the instrument is much less affected by external temperature variations, and only one of these is exposed to the infra-red radiation. Directions for making one of these instruments are given by Schaeffer, Paulus, and Jones,[3] and the following details are quoted from their paper. The thermo-junctions are made of the Hutchins alloys, which consist of ninety-seven parts of bismuth and three parts of antimony, and ninety-five parts of bismuth and five parts of tin respectively. A central wire of the second alloy was sealed at each end to wires of the first alloy and the two wires of the first alloy were sealed to the wire loop which consisted of No. 36 wire of the purest copper attainable. This wire was previously treated with strong nitric acid to remove from the surface any magnetic contamination. Each thermo-junction carried a tiny vane, 2×2 mm. square, coated with lamp black. Greater sensitivity can be obtained with only one junction but the advantages gained from the use of the compensating type of junction are well worth the sacrifice in sensitivity. It is very important that the weight of the junction be kept as small as possible, not only to lessen the weight of the suspended system, but especially to reduce the heat capacity of the junction to a minimum. A small heat capacity insures a quick acting suspension, and one which will return more rapidly to the zero point. In the instrument described the weight of the completed compensating junction was 0·0029 gram. The plane mirror attached to the suspension was very thin and had an area of about 20 sq. mm.

The whole was suspended by a quartz fibre 30 cm. in length, this length being a material aid in eliminating vibrations. The authors state that this instrument was very satisfactory in its behaviour, the free-

[1] *Bureau of Standards, Bulletin*, 9, 7 (1913).
[2] *Phys. Rev.*, 34, 228 (1912); *Phys. Zeitsch.*, 13, 870 (1912).
[3] *J. Amer. Chem. Soc.*, 37, 776 (1915).

dom from vibration being proved by the steadiness of the light spot on a scale at a distance of 12 feet.

One of these instruments has been constructed by Mr. G. Nodder, at Liverpool, and Professor Lewis has employed it with success in some investigations of absorption spectra in the short wave region in the infra-red.[1]

Whilst the pioneer work in the infra-red has been carried out by means of the four types of the recording instruments, bolometer, radiometer, radiomicrometer, and thermopile, a few words may be said as to the best instrument to be used by those who wish to undertake work for themselves in this region. It will be evident to all who read the literature on the subject that, whereas extraordinarily fine work has been carried out by the aid of each of these instruments, this work has been that of scientists who have served a long apprenticeship and are specialists of the highest order. Each has succeeded in constructing apparatus of the greatest delicacy and if everyone had to make for himself his own recording instruments the task might well alarm even the most courageous. During recent years experience has become more crystallised, with the result that instruments are on the market which possess a very high degree of sensitiveness and with which work of great precision can be carried out.

As regards the choice of recording instruments there is little doubt that the thermopile has been so much improved in sensitivity that it forms one of the best, if not the best, instrument for use in the infra-red. Some may feel a preference for one of the other instruments but I myself believe that the one which is the most suitable and most likely to become the standard instrument is the thermopile. It may be stated too that Coblentz has modified the opinion he expressed earlier as to the relative merits of the four instruments and now believes that the thermopile is the best of all. To this it may be added that in practically all modern work the thermopile is used as the recording instrument.

The general principles laid down by Johansen have been adopted by the Adam Hilger Company, who have succeeded in making thermopiles which are exceedingly well adapted for work in the infra-red. The original investigations have been supplemented by further experiments on the distribution by convection, conduction, and radiation of the energy received by the thermopile. As a result it is possible to calculate for each size of thermopile the number of elements, dimensions of the lead wires, etc., to produce the maximum sensitiveness. In the most modern form of the instrument the Hutchins alloys (see p. 250) are used. The thermopile is singularly free from "creep" and is adapted for use with the most sensitive galvanometers. The instrument is made in three sizes, the widths of the sensitive area being 1·5 mm., 1·0 mm., and 0·5 mm., respectively. The resistance of this type of thermopile is of the order of 10 ohms, and for the maximum sensitivity to be realised it is advisable that the resistance of the galvanometer

[1] H. A. Taylor and W. C. McC. Lewis, *Trans. Chem. Soc.*, **121**, 665 (1922).

should not differ largely from that of the thermopile. An illustration of one of these thermopiles is shown in Fig. 124.

Coblentz in much of his recent work, not the least interesting of which has been the measurement of the energy received from the stars, has used a vacuum thermopile of his own design, the thermo-junction being bismuth-silver.[1] He points out that in addition to the increased sensitiveness normally gained by mounting the instrument in vacuo there is the added advantage that the galvanometer mirror is much steadier, owing to the absence of convection currents within the cell containing the thermopile. He has recently[2] adopted the method of having a side tube, containing metallic calcium, attached to the apparatus. After the vacuum has once been established it is only necessary to heat this tube occasionally, which can readily be done by electrical means. This method very materially increases the portability of the instrument.

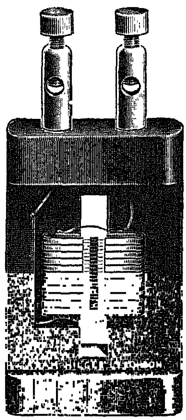


FIG. 124.

Another type of thermopile has been designed and used by Moll,[3] who points out that all improvements in the construction of this instrument have been designed to increase its sensitivity and that little or no attention has been paid to the question of rapidity in action. The greater this rapidity, the better is the instrument adapted to the investigation of all types of radiation phenomena of short duration and rapid variability. Further, great rapidity in action leads to great stability of the zero, and its indications will therefore be the more certain, the more quickly they are arrived at.

The rapidity of a thermopile is determined by the rapidity with which a difference in temperature of the junctions comes to an equilibrium, a process in which not only the heat capacity of the junctions plays a part, but also and chiefly the heat exchange by conduction, radiation, and convection. Heat exchange also takes place while the instrument is exposed to the radiation, and thus will have a directly prejudicial effect on the sensitivity. If, therefore, this exchange be furthered in order to increase the rapidity, a diminution in sensitivity will result unless it be arranged to compensate this in some other way. In a surface instrument the two conditions can be satisfied and Moll has constructed such an instrument, in which both great rapidity and great sensitivity have been attained.

The thermopile is built up of a great number of strips, partly of constantan and partly of copper, and these strips are soldered at each end to a copper bar. The constantan-copper strips can be exposed throughout their whole length to the radiation. On account of the

[1] *Bureau of Standards, Bulletin*, 13, 444 (1916-17).
[2] *Bureau of Standards, Scientific Papers*, 17, 187 (1922).
[3] *Konink. Akad. Wetensch., Amsterdam, Proc.*, 16, 568 (1913).

great difference in the heat capacity of the two junctions, namely, that between the two sections of each strip and that between the constantan strip and its copper bar, the former will attain a higher temperature than the latter, the equilibrium of temperature being reached in a very short time owing chiefly to the good heat conduction between the junctions. Since copper and constantan differ considerably in their conductivity, the strips of these two metals are made of different thickness and length, so that the temperature may be highest at the junction between the strips while the strip is exposed to the radiation.

Elements, such as described, may readily be combined to form a pile. Moll combined 80 of these, arranged in three rows of 24, 32, and 24, respectively, the whole filling a circular surface of 2 cm. in diameter. The total resistance was 9 ohms and the sensitivity and

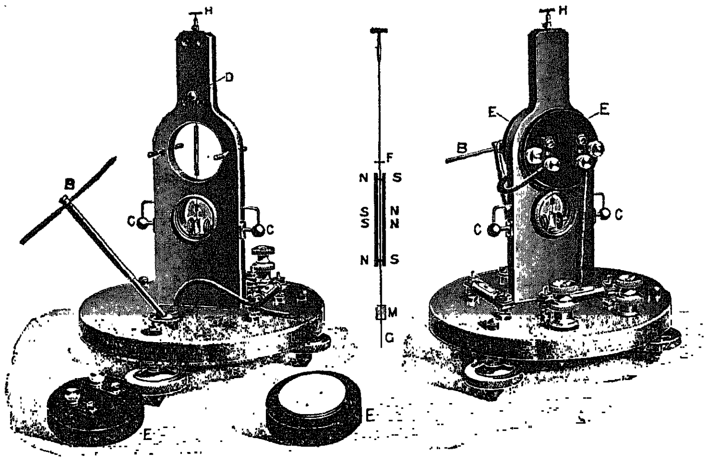


FIG. 125.

rapidity of action were great. A standard candle at 1 metre distance gave an E.M.F. of 18 micro-volts, the current reaching 99 per cent. of its full value in 1·5 seconds.

Similar elements may also be combined to form a linear thermopile, but, since in this case the exposed surface is narrow, such an instrument becomes less sensitive. A linear thermopile of 30 elements was compared with one of the Rubens instruments. The two had equal resistance (3 to 5 ohms) and in the case of equal surface (20 × 1 mm.) the Moll thermopile was about 20 per cent. less sensitive. This disadvantage was amply compensated for by its rapidity in action, which was four times as great.

For use with the thermopile there are three galvanometers which may be described, namely, the Broca, Paschen, and Moll instruments. The distinctive feature of the Broca galvanometer is in the moving system. The magnets consist of two steel wires placed vertically, and

each so magnetised that its two ends are of like polarity with a consequent pole in the middle. It is thus possible to use comparatively powerful magnets, whilst the moment of inertia is kept small; at the same time the arrangement is very astatic. The whole system is suspended by a fine quartz fibre. The instrument is shown in Fig. 125, the controlling magnet being shown at B. The faces of the ebonite coil boxes, E, E, are completely covered by a thin metallic shield, the frame also being of metal, so that the suspended system is completely shielded from electrostatic forces. In order to guard against a large potential difference between the metal frame and the coils, one terminal is connected to the frame. The instrument is insulated by ebonite toes fitted to the levelling screws. The sensitivity of the instrument is shown by the following data obtained with some recent galvanometers:—

Resistance of coils in series in ohms.	Period in seconds.	Deflection in mm. at 1 metre		1 mm. deflection at 1 metre produced by		Factor of merit.
		per micro-amp.	per micro-volt.	micro-amps.	micro-volts.	
8·8	10·0	350	40·0	0·0029	0·025	147
8·8	17·3	1070	121·0	0·00093	0·0083	150
110	10·0	1000	9·1	0·001	0·11	153
110	17·3	3000	27·3	0·00033	0·037	159
860	10·0	2200	2·6	0·00045	0·38	148
860	17·3	6500	7·5	0·00015	0·13	146

The factor of merit given in the last column is given by—

$$\text{Factor of Merit} = \frac{100 \times D}{T^2 (R)^{2/5}} \text{ or } \frac{100 \times D_1 \times R^{2/5}}{T^2}$$

where T = Periodic time (undamped) in seconds,
R = Galvanometer resistance in ohms,
D = Deflection in mm. per micro-ampere at a scale distance of 1 metre,
D_1 = Deflection in mm. per micro-volt at a scale distance of 1 metre.

The Paschen galvanometer is shown in Fig. 126 and is developed from the instrument Paschen employed with his bolometer. The moving system consists of two groups of thirteen magnets, arranged alternately on opposite sides of a fine glass stem. The complete moving system weighs only 0·003 grams. A special feature of this galvanometer is to be found in the winding of the coils. These are wound in pairs and are designed to produce the maximum field for a given resistance of copper, which is secured by winding the coils with six sizes of wire, beginning at the centre with the smallest and finishing with the largest. The coils are wound in an elliptical shape, which permits the use of a

reater number of magnets and produces a field of more efficient shape. 'he sensitivity of this instrument, which is about forty times that of the Broca galvanometer, is shown in the following table :—

Resistance in ohms.	Period in seconds.	Deflection in mm. at 1 metre produced by		1 mm. deflection at 1 metre given by		Factor of merit.
		1 micro-amp.	1 micro-volt.	micro-amps.	micro-volts.	
12·23	6	8560	700	0·000117	0·0014	8720
3·0	6	3900	1300	0·000256	0·00077	6980
0·75	6	2080	2773	0·00048	0·00036	6500

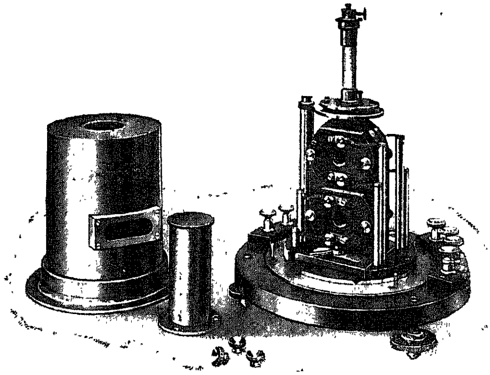


FIG. 126.

The third type of galvanometer was designed by Dr. Moll[1] in Professor Ornstein's laboratory at Utrecht and is illustrated in Fig. 127. t has a moving coil in an electromagnetic field, the mirror is a plane one, and when used with a lens gives very good definition, it being possible with a pointolite lamp to read to 0·25 mm. at a working distance of 3 to 4 metres. The resistance of the coil is about 64 ohms. The instrument is very quick in its action: in approximately 1·5 seconds the coil reaches its final position within less than 1 mm. for a total movement of 200 mm. The sensitivity is shown in the following table :—

Deflection for 1 micro-ampere at 1 metre . .	200 mm.
Deflection for 1 micro-volt at 1 metre . . .	3·06 mm.
Creep after 10 minutes deflection of 200 mm.	3·0 mm.
Resistance of coil	64·75 ohms.
Period	1·5 second
Field coil resistance	3·25 ohms.
Figure of merit	1670

[1] *Konink. Akad. Wetensch., Amsterdam,* 16, 149 (1913).

Mention may be made of another galvanometer, the manufacture of which is in the hands of Leeds and Northrup of Philadelphia. This instrument has been designed by Coblentz and is based on investigations carried out by him over some years.[1]

A few remarks may be appended on the use of a highly sensitive galvanometer and the results given of some experience with the three instruments just described. In the first place, there is the question of mechanical vibration which unfortunately is a matter of great importance in some laboratories. It is as a rule recommended that a galvanometer be placed on a shelf resting on brackets fixed to one of the walls of the laboratory. It happens that in the Liverpool laboratories the mechanical

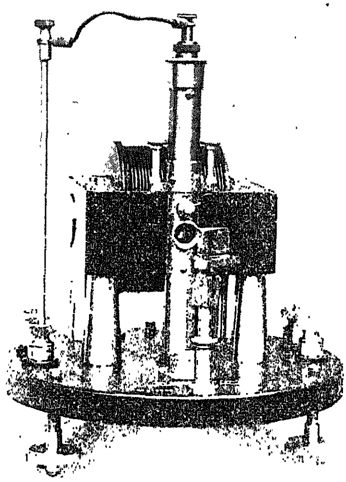


FIG. 127.—Moll Galvanometer.
(*The Cambridge and Paul Scientific Instrument Company, Ltd.*)

vibration causes considerable trouble owing to the fact that the buildings rest on sandstone, which is pierced by two railway tunnels, and heavy trains are passing through these at frequent intervals. Using a Broca galvanometer mounted as above it was perfectly easy to detect the thrust on the driving wheels of the locomotive when a heavily laden passenger train was started at Lime Street station at about 800 yards distance. No better results were obtained by the adoption of the device of a board suspended by three wires from a bracket on the wall. Much greater stability, however, was gained by mounting the galvanometer on a wooden plate resting on three tennis balls, a method suggested by

[1] *Bureau of Standards, Bulletin*, **9**, 56 (1913), and **13**, 423 (1916-17).

Professor Wilberforce. This method has also been tried with success in the case of the Paschen instrument.

The second difficulty, and by far the greater, is the disturbance due to external magnetic fields. The Broca galvanometer, in spite of the astatic type of the suspended magnet system, is much more readily affected than might be expected. It was found for instance that one of these instruments was effectively disturbed by a spark discharge in a neighbouring laboratory and consequently this instrument could not be used, without being shielded, for the measurement of the emission spectra of elements. Of the three galvanometers described above the Broca is the least satisfactory, since it is questionable whether in view of its relatively small sensitivity it is worth the trouble and expense of shielding.

The Paschen galvanometer is of course the most sensitive instrument and as a result of this it is an exceedingly difficult instrument to use in a town laboratory. In order to minimise the disturbances the makers recommend the use of two concentric soft iron conical shields which are placed over the instrument, holes being cut in these to allow the passage of light to and from the galvanometer mirror. Although it is true that the suspended magnet system is of the astatic type this instrument is readily affected by external fields.

In the use of a highly sensitive galvanometer, provided that mechanical vibration is entirely eliminated, there are three troubles which manifest themselves, namely :—

(1) Unsteadiness of the zero.
(2) Drift of the zero.
(3) Change of sensitivity.

Of these the first can be obviated by the use of an efficient shield and by the complete protection of the thermopile from the effects caused by convection currents. The latter may be secured by the use of a vacuum thermopile. The second difficulty is the greatest and necessitates a constant adjustment of the control magnet, which naturally changes the sensitivity of the instrument. Under the conditions frequently to be found in town laboratories the drift of the zero is so variable and troublesome that any approach to real accuracy seems to be unattainable. For example, two of these instruments have been tried at Liverpool at different times, and in spite of the utmost care and by working only during the night it must regretfully be stated that it was found impossible to obtain accurate results by the ordinary method.

On the other hand, Dr. Rebekoff, working in Professor Allmand's laboratory in King's College, London, has succeeded in using this instrument by a "null" method.[1] He had previously found that the drift of the zero was so great as to preclude the use of the instrument in the ordinary way.

The galvanometer was mounted with its shields in position and the

[1] Private communication.

magnetic field set up in the galvanometer by the thermo-electric current from the thermopile was opposed by a field established through the shields by a current of known amount passed through a coil placed outside the shields, this coil being placed at right angles to a line passing through the galvanometer. The magnitude of the current was adjusted by a variable resistance until no shift of the galvanometer zero could be detected. It had previously been found that the galvanometer deflection was proportional to this current and, therefore, the intensity of the radiation falling on the thermopile was measured, not by the magnitude of the galvanometer deflection, but by the magnitude of the current through the coil. The results obtained in this way are independent of the sensitivity of the galvanometer and this was experimentally proved to be the case.

In order to use this method with success, the opposing current through the coil must be switched on at the same instant that the thermopile current comes into action. In order to achieve this a special switch was used which closed the coil circuit and raised the shutter protecting the spectrometer slit at the same instant. A definite time, however, elapses between the raising of the shutter and the development of the thermopile E.M.F. This could partially be corrected for by adjustment in the contacts of the switch, but owing to the difference between the time curves of the thermopile and coil a small fluctuation always occurs, even when the opposing current is of the correct dimensions, before the spot of light settles down.

It is best not to employ too great sensitivity in the galvanometer in this method. A high sensitivity means a long vibration period for the mirror and hence a longer initial period during which magnetic disturbances may occur and alter the zero of the instrument.

The Moll galvanometer possesses a great advantage over the two other instruments in that it is extraordinarily little disturbed by vibration or external magnetic fields. When placed on a table in an ordinary laboratory it is not affected by the vibrations of the building even when the laboratory is on one of the upper floors. I have seen several of these instruments in use at Utrecht and despite the ordinary traffic, electric trams, etc., the spot of light in each case was perfectly steady. As can be seen from the description of this instrument given above, its sensitivity is much higher than that of the Broca instrument and about one-sixth of that of the Paschen galvanometer. In view of the abovementioned advantages and of its rapidity of action it would seem that this galvanometer is the most promising for use for infra-red work in a town laboratory.

It might perhaps be considered that the foregoing remarks are uncalled for and that in view of the beautiful results that have been obtained by the use of highly sensitive instruments it is only a question of care and patience to be able to gain results of equal accuracy and value. This is not necessarily true, since some are tied by circumstances to laboratories situated in close proximity to electric trams, railway trains, *et hoc genus omne*, not one of which is conducive to rest

ıd peace as far as galvanometers are concerned. The notes, born of ıd experience, are written not for those fortunate enough to work in .aces more free from disturbing influence but rather for those who, ıough by fate condemned to work amidst such disturbances, are enıusiastic enough to aspire to research and hope to succeed in spite of ıe ills that beset them.

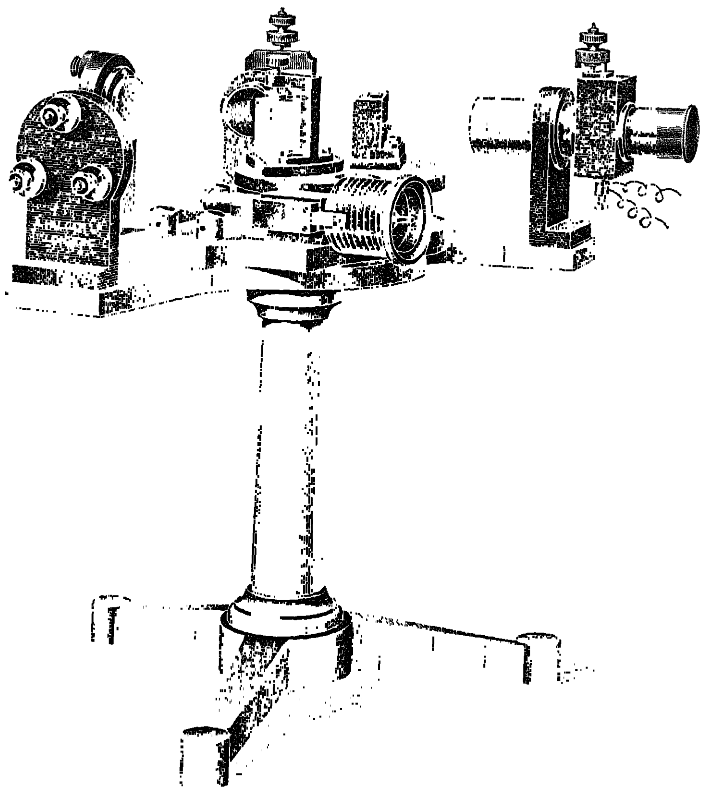


FIG. 128.

A few words may also be added about the dispersing instruments to be used in this region. For work up to the wave-length of about 10μ a prismatic instrument may be used, the prism being of rock-salt and the lenses replaced by mirrors. A constant deviation instrument of this type has been devised by a modification of the monochromator shown in Fig. 56. This instrument, which is direct reading, is shown in Fig. 128, concave mirrors being substituted for the collimating and telescope lenses. The light entering the first slit is collimated by the first

mirror and passes through the rock-salt prism to the plane mirror. It is reflected thence to the second concave mirror, by which the spectrum is focussed on to the second slit, and immediately behind this slit is placed the thermopile. The prism and plane mirror are mounted on a table which is rotated by a fine screw carrying a drum on which the wave-lengths can be directly read. The three mirrors are made of glass heavily coated with gold or platinum by electro-deposition.

In using this instrument or any other design with a rock-salt prism great care must be taken to guard against damage to the prism by moisture, owing to the fact that rock-salt is hygroscopic. The prism should never be left in position when the instrument is not in use. In this type of spectrometer the prism must be mounted on a support which can readily be removed from the prism table and replaced thereon in proper orientation when required. Such an arrangement is shown in Fig. 128, where the prism support carries three screws which rest in three radial grooves on the prism table. When not in use the prism and its support must be kept in a desiccator and the most important precaution to take is that, when the prism is taken out of the desiccator and mounted on to the spectrometer, its temperature is not lower than that of the instrument. Professor Lewis at Liverpool has found it an excellent plan to place the desiccator on a brick resting on supports on the laboratory bench. An inch or two under the brick a small gas flame about one-quarter inch high is always kept burning. This arrangement maintains a constant temperature one or two degrees above that of the laboratory, with the result that no film of moisture ever forms on the prism when it is brought out of the desiccator and placed in position. The small difference in temperature has no effect on the resolving power of the spectrometer. If this plan is adopted, there is no need to keep the air dry, and indeed it is better not to have any drying agent present.

In the instrument described above the prism is usually coated with a very thin film of varnish by dipping it in a solution of pyroxylin in amyl acetate. This serves as an excellent protective coating but, though most of the rays up to 10μ are transmitted without sensible absorption, the pyroxylin has one well-marked absorption band in this region. By the use of the Lewis device this varnish is rendered unnecessary and if a prism has been coated the film may be removed by washing with amyl acetate.

The adjustment of this instrument is very similar to that described previously on page 130, but of course the standard wave-lengths are different. It is possible to adjust the direct reading instrument by the use of some visible radiation, such as that of sodium. Both slits are closed to their working width and the reading on the drum is set to the correct reading and then, the thermopile being removed, the radiation should be seen on looking through the second slit. This is not very satisfactory as the correct adjustment is made at one extreme end of the spectrum range. It is far preferable after such preliminary adjustment has been carried out to make the final test by means of some definite and known radiation nearer the middle of this range. For this

purpose the emission bands of carbon dioxide given by the bunsen flame at $4{\cdot}32\mu$ aud $4{\cdot}43\mu$ may be used. It must be realised that such radiation is not sharply defined like a spectrum line, but is in the nature of a broad band, the wave-length given being that of the position of maximum intensity. In using such a band, therefore, the throw of the galvanometer mirror is observed at close intervals on the wave-length scale, commencing on one side of the band and passing through the maximum. The intensities as registered by the galvanometer throw are plotted against the wave-lengths and from the curve the wave-length of the maximum intensity can be obtained. This must agree with the known value.

When it is required to investigate the regions of much longer wave-length than 10μ then it is advisable to use a grating instrument and there is no standard design of instrument on the market for this type of work. Sufficient has possibly been said of the methods that have been used by various experimenters in the different regions to render it possible for anyone to construct a spectrometer for his own use. In the case of such an instrument the measurement of the angular deviation is the essential feature, and any well-designed spectrometer may be used with a grating specially ruled or wound for the particular region to be investigated. It must be remembered that, whilst a telescope carrying a slit and thermopile may be moved for the purpose of exploring the region defracted by a grating in fixed position, such is not possible if a radiomicrometer or radiometer is used. This type of recording instrument should be used with a fixed arm spectrometer, the spectrum being made to travel across the slit by rotation of the grating.

The Extreme Ultra-Violet Region.—It was described in the introduction how the discovery of the ultra-violet region was made first by Ritter and by Wollaston. This region was first photographed by E. Becquerel by projecting it upon paper coated with silver chloride, when he observed the continuance of the Fraunhofer lines as far as he was able to reach in this region. Investigations were carried out in this region by Stokes,[1] who made use of a quartz prism apparatus, and observed the spectrum visually by projecting it upon a fluorescent screen. He observed in this way the solar spectrum to about $\lambda = 3000$, which is the limit set by the absorption of the rays by the atmosphere. The spectrum of the electric spark, however, he traced much further, and found that aluminium in the spark emitted rays of the smallest wave-length he was able to reach—in fact, he observed the pair at $\lambda = 1862$ and $\lambda = 1854$ A. Mascart was the first to make measurements in this region by means of photography, which he succeeded in doing with the help of gratings. These gratings he placed always in the position of minimum deviation (see p. 179), and by means of an ordinary spectrometer, with a small camera put in place of the eyepiece, he took photographs of very small regions of the spectrum. The cross wires were not removed from the eyepiece, and they therefore cast a shadow upon the

[1] *Phil. Trans.*, **142**, 463 (1852), and **152**, 599 (1862).

plate at the point corresponding to the reading of the telescope upon the divided circle of the instrument. From this he was able to measure the angular deviations of the various lines, and thus obtain their wave-lengths. The actual determinations were not particularly accurate. Attention may, however, be drawn to the fact that Mascart and also Soret fixed upon certain lines in the spectra of cadmium and other elements, and numbered them as standards of reference. These lines, especially those in the ultra-violet, are often referred to by their numbers, so they may be given here with their wave-lengths on the international scale:—

Designation.	Wave-length.	Designation.	Wave-length.
Cd 1	6438·47	Cd 16	2836·91
Cd 2	5379·00	Cd 17	2748·6
Cd 3	5338·30	Cd 18	2573·06
Cd 4	5085·83	Cd 19	2499·83
Cd 5	4799·91	Cd 20	2469·77
Cd 6	4678·15	Cd 21	2418·74
Cd 7	4415·68	Cd 22	2321·16
Cd 8	{3988·3 3984·6	Cd 23 Cd 24	2312·82 2265·03
Cd 9	{3612·89 3600·51	Cd 25 Cd 26	2194·63 2144·39
Cd 10	{3467·63 3466·20	Zn 27 Zn 28	2099·9 2061·92
Cd 11	3403·60	Zn 29	2025·4
Cd 12	3283·81	Al 30	1989·84
Cd 13	3133·2	Al 31	1935·23
Cd 14	{3084·86 3080·91	Al 32 Al 33	1862·15 1854·04
Cd 15	2980·65		

Somewhat similar methods were used by Cornu, Liveing and Dewar, and by Hartley and Adeney, in their work on wave-length determination in this region. The actual work does not require more than this brief mention, because it can hardly be considered as more than of historical interest, since more recent measurements are far more accurate.

At the present time experimental work in the ultra-violet to as far as $\lambda = 2150$ A. is perfectly simple, owing to the fact that the ordinary photographic plate is sensitive to this region, so that it is an easy matter to work in this region either with a quartz prism spectrograph or a concave grating instrument. As was stated on page 37 the wave-lengths of the secondary and tertiary standards do not at present extend beyond the limit of 3370 A., but the wave-lengths of the iron lines up to 2375 A. have been recommended for use on page 133. For work between 2375 A. and 2150 A. other wave-lengths must be used, with of course a sacrifice in probable accuracy.

The limit reached in a spectrograph depends on three factors, namely, the absorption caused by the dispersing medium in the case of a prism spectrograph, the absorption due to air, and the decrease in sensitivity

of the ordinary photographic plate. The limit with the type of instrument used for accurate work certainly does not lie beyond 2150 A., although in the case of the instrument shown in Fig. 61 on page 117 it is possible to reach 1850 A., but owing to the small dispersion the accuracy of work is considerably reduced. The limit is usually accepted as being near to 2150 A. and there is no necessity for a description of work up to this limit for it differs in no way from that given in Chapters V. and VII.

The three absorption factors mentioned above all become effective at or about the same region in the spectrum, and consequently little use is, in general, served by eliminating any one without the other two. It will, however, be found that the greatest effect is caused by the absorption of the gelatine in the photographic plate and consequently there is a rapid fall in sensitivity towards the short wave-lengths. This effect is noticeable even at the wave-length of 2250 A. and the use of the special Schumann plate very materially increases the intensity of the lines photographed between 2250 A. and 2150 A. Except for certain absorption spectra observations it is questionable whether the advantage gained is worth the extra expense involved.

For the extension of the spectrum beyond the limit of 2150 A., we are indebted to Schumann, Lyman, McLennan, and Millikan, the last named having succeeded in observing emission spectra to 136 A. The first step was made by Schumann who eliminated the absorption due to the air and to the gelatine by the use of a vacuum spectrograph and photographic plates having very little or no gelatine. Schumann used a fluorite prism and in this way reached an estimated limit of 1200 A. He could not measure the wave-lengths of the spectrum lines which he discovered because the dispersion curve of fluorite in that region was then unknown. The existence, however, of a new spectral region was definitely established by him and it is owing to his pioneer work that the later investigations were undertaken. The next step was taken by Lyman who by the substitution of a concave grating for the fluorite prism was able not only to simplify the apparatus but also to determine the wave-lengths of the spectrum lines. He found that the limit of transmission of fluorite lies at about 1200 A. and that Schumann's observations did not extend beyond that point.

The apparatus used by Schumann is of considerable interest. He described two instruments, the second being a perfected form of the first.[1] It is not necessary to describe the apparatus in detail but the following brief description may be given:—

Schumann pointed out that the whole apparatus must be exhausted, and that the following adjustments must be so arranged as to be controllable from outside the apparatus, without disturbing the vacuum: (1) rotation of the slit round the collimator axis; (2) the width of the slit; (3) the length of the slit; (4) the position of the effective slit aperture, this adjustment being for the purpose of taking adjacent

[1] *Wien. Ber.*, **202**, IIA, 625 (1893).

spectra upon the plate for wave-length determination; (5) focussing of both collimator and camera lenses; (6) adjustment for minimum deviation; (7) adjustment of the angle between camera and collimator, so as to enable different regions of the spectrum to be photographed; (8) adjustment of the tilt of plate in the camera; and (9) movement of the plate in a vertical plane. All these adjustments Schumann arranged for in his instrument, which may be briefly described as follows:—

Fig. 129 is a diagram of the principal part of the system, namely, the central bearing, in sectional deviation; *a* is the central cone, which is firmly screwed to the centre of a strong tripod stand, *d*, a locknut being shown at *e*. This cone is bored out in the centre, and forms the prism chamber; it has a cover, *c*, accurately fitted upon the top. Over

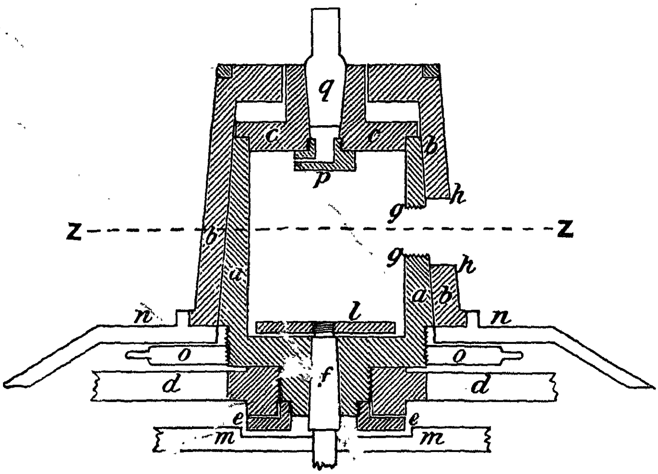


FIG. 129.

the outside of the cone *a* is fitted the hollow cone *b*, which is accurately ground upon *a*, so that a perfect fit is obtained all over the surface. The collimator tube is fastened to the inner cone *a*, whilst the camera tube is fastened to the outer cone *b*; this allows the latter to be rotated round the central vertical axis of the instrument. The method of attachment of the collimator and camera tube is shown in Fig. 130, which is a diagram of a horizontal section cut along the dotted line ZZ of Fig. 129.

The collimator is screwed into the inner cone *a* at *g*, and the outer cone *b* is slotted from *h* to *h* to permit of its rotation within the necessary limits; the telescope is screwed on to the outer cone *b* at *i*, whilst the inner cone is slotted from *k* to *k*, to allow the passage of the rays from the prism.

As will be seen in Fig. 129, the bottom of the inner cone *a* is

conically bored, and into this is fitted the plug *f*, which is screwed into the disc *l*; the plug *f* is held in position by locknuts to prevent its falling out when the apparatus is not exhausted. The disc *l* is the platform upon which the prism table rests; this may be rotated by turning the plug *f*, which may readily be done by means of a large milled head upon its lower end. The two arms *m*, *m* are fixed to *f*, and are fitted with verniers reading upon a divided circle, so as to enable the position of the prism to be read at any time. A similar purpose is served by the arms *n*, *n*, which are provided with verniers reading upon the same divided circle; these give the rotation of the camera tube, and hence the angle of deviation. Attention may be drawn to the ring *o*, which is screwed on to the inner cone *a*, and is provided with lugs; by screwing up the ring *o* one is enabled to raise the outer cone off the inner one, if by any chance it has become fixed by remaining in one position too long.

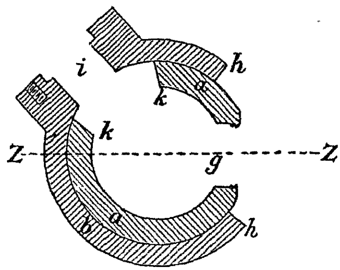


FIG. 130.

The upper lid *c* is conically bored in the centre, and the glass tube *q* is ground therein; this tube connects directly with a mercury pump; a

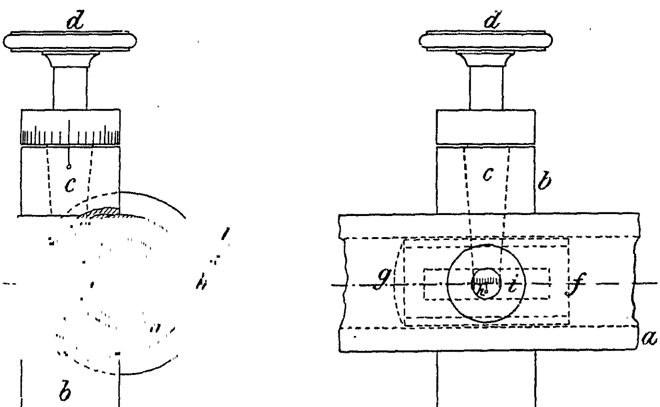


FIG. 131.

plug is screwed in at *p* to restrain the flow of air when the apparatus is suddenly exhausted or opened when vacuous to the atmosphere.

A diagram of the arrangement for focussing is shown in Fig. 131, in plan and end elevation. *a* is a portion of the collimator or camera tube, and *b* is a round metal block soldered to the side. The plug *c* is ground

into a conical hole drilled in *b*, and carries a pinion wheel, *e*, which engages in a rack, screwed to the inner tube *f*, which carries the lens at *g*; the plug *c* is fitted with a milled head, *d*, whereby it may be turned. In order to know the position of the inner sliding tube *f*, on the opposite side of the tube *a* is a hole cut at *h*; and this is hermetically sealed with a glass plate *i*; the sliding tube is ruled in millimetres, and its position may be read off against a zero mark upon the tube *a*.

The camera itself very much resembles a stop-cock placed in a vertical position. Fig. 132 represents the camera in sectional elevation, and Fig. 133 a horizontal section through the axis of the telescope tube, *i.e.* through the line XX. The outer barrel of the apparatus is shown at

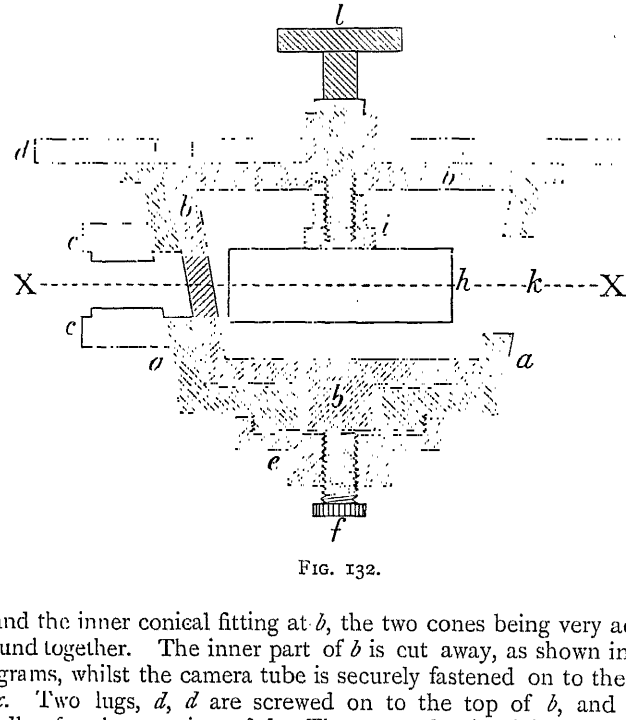


FIG. 132.

a, and the inner conical fitting at *b*, the two cones being very accurately ground together. The inner part of *b* is cut away, as shown in the two diagrams, whilst the camera tube is securely fastened on to the barrel *a* at *c*. Two lugs, *d*, *d* are screwed on to the top of *b*, and serve as handles for the rotation of *b*. The top of *a* is divided for a short distance in degrees to enable the rotation of *b* to be measured. On to a projection under *a* is screwed a nut *e*, into which again *f* is screwed; this, as before described for the main conical bearing, is for the purpose of loosening the cone *b* if it has got jammed in *a*.

For the vertical motion of the plate the following device is adopted: On the back of the opening in *b* is a long vertical slide running from top to bottom—this is not shown in Schumann's diagram, but may be represented by the slotted pieces *g*, *g* (see Fig. 133). The sliding piece

in these two ways is fastened to a frame, *h* (Fig. 132), into which slides the plate-carrier. This sliding piece is also fastened to the nut *i*, in which works the screw *m*, which forms part of the plug *l*. This plug *l* is ground into a conical hole bored in the top of the inner cone *b*. Thus, by simply rotating this plug, the plate can be raised or lowered as required; the amount it is raised or lowered can be directly read off upon a scale by means of a divided drum, not shown in the diagram. The slot *k* cut in the outer cone *a* is for the purpose of putting in or taking out the plate carrier, which is done by means of a key. In the diagrams the inner cone *b* is so turned that the plate may be put in; when this has been done *b* is turned round so as to bring the opening opposite to the camera-tube end, and set the plate at the proper angle to the axis of the camera lens. The plate carrier has no cover, and therefore the changing of a plate must be done in the dark or ruby light.

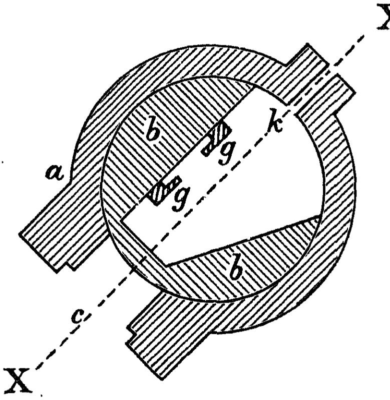


FIG. 133.

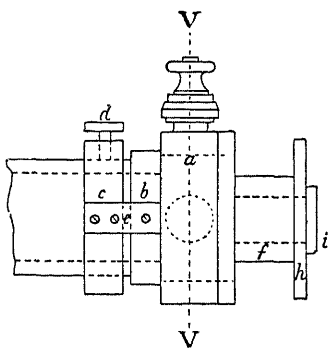


FIG. 134.

The size of plates actually used by Schumann is 37 × 12·5 mm., and the amount of possible vertical shift that can be given to the plate is 9 mm.

The slit is a very complex mechanism, and is shown in Figs. 134 and 135; the former is a diagram of the apparatus in elevation, and the latter a view of the slit mechanism obtained by cutting a section through the line VV. In Fig. 135 only the essential parts are shown, as Schumann's drawing is very complicated, and hardly suited for reproduction. The main chamber containing the slit mechanism is shown at *a*; the plate *b*, which is securely screwed to *a*, is ground flat on the outer face, and this is held up against the similarly ground end of the collimator tube; a small quantity of grease makes a perfectly air-tight joint. The slit is centred and held in position by the collar *c* and the set-screw *d*, the former being fastened to the plate *b* by two straps, one of which is shown at *e*. The slit cover consists of a tube, *f*, which also has a ground end, and is thus held by the atmospheric pressure

against the slit chamber *a*. The plate *h* is screwed to the end of the tube *f*, and *i* is a fluorite plate cemented on to *h*. The reason for these fittings will be given below. The slit mechanism proper is shown in Fig. 135, and consists of a vertical and horizontal slit; the vertical slit, or slit proper, consists of one fixed jaw and one jaw movable by a micrometer screw; the horizontal slit also consists of one fixed and one movable jaw, but there is an additional arrangement by which the whole of this slit can be bodily moved without altering its width. The two slits are immediately behind one another, there being about 0·01 mm. clear-

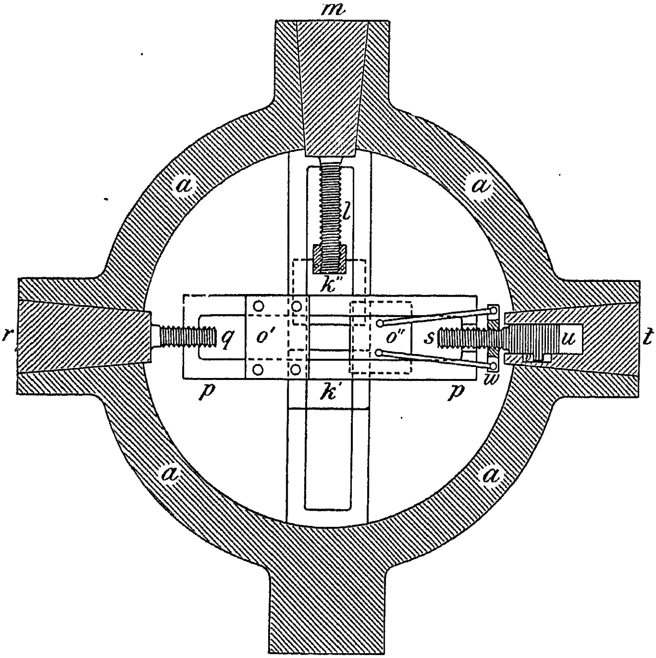


FIG. 135.

ance between the two sets of jaws. Inside the frame *a* is a strong back plate, on which the jaws are mounted, but this plate is not shown in the diagrams; the jaws of the vertical slit are shown at *k'k''*, and these are fitted in grooves mounted on the back plate. When the apparatus is mounted, it is so placed that the edges of the jaws *k'k''* are parallel to the refracting edge of prism. One of the jaws, *k'*, is screwed to the back plate, whilst the other is moved by the micrometer screw *l* with a pitch of 0·2 mm., which projects from the taper plug *m*; this plug, like all the others, is carefully ground into a conical hole bored in *a*, and is provided with the usual apparatus for measuring its rotation.

The jaws of the horizontal slit are shown at *o'* and *o''*, and are fitted

to grooves on the frame *p*, which works in grooves on the back plate; the micrometer screw *q*, of 0·5 mm. pitch, works in a nut fastened to *p*, so that by turning the taper plug *r* the frame *p* carrying the whole horizontal slit can be moved to and fro. The micrometer screw *s*, of 0·2 mm. pitch, also engages in a nut on the frame *p*, but does not form part of the taper plug *t*; this plug *t* is centrally bored for some distance, and in this hole fits the cylinder *u*, which is an extension of the micrometer screw *s*. On the side of *u* is a small pin, *v*, which slides in a groove cut in the inside of the plug *t*. It thus follows that when *t* is turned the screw *s* is made to revolve; but when by means of the plug *r* the frame *p* is made to travel backwards or forwards, the cylinder *u* simply slides in or out of the boring in the plug *t*. There is a small ring, *w*, fitted to the spindle *su*, which is connected by a light framework to the movable jaw o''; the ring *w* does not rotate with the screw *s*, and is held in position by a collar on each side, so that when *s* is screwed in or out of its nut on the frame *p*, the jaw o'' is moved in or out. Each of the plugs is fitted with an apparatus for measuring the rotation, and in this way the travel of the slit jaws can be found at any time; further, on the plug *m* there is a stop fixed so that the jaws cannot be brought into contact; this stop, in Schumann's apparatus, limits the width of the slit to 0·007-·02 mm., which is quite sufficient for ordinary work, but if required the stop may be removed and wider slit breadths obtained. These two diagrams of the slit give all the essential points of Schumann's arrangement, but of course certain details are omitted, such as the springs to obviate the backlash of the screws, the slit grooves, etc. For more complete designs the original memoir must be consulted.

Only one detail of construction now remains to be described, namely, the arrangement by means of which the rotation of the various taper plugs controlling the different adjustments is measured. These are shown in sectional and ordinary elevation in Figs. 136 and 137 respectively. The taper plug is shown at *a*, and the divided drumhead at *b*; this is accurately fitted to the plug *a*, and is fastened thereon by the nut *c*. Fitting accurately upon the outer cylinder *e* is a double-walled ring-piece, *d*, upon which a screw-thread is cut which engages, as shown, into a similar thread cut upon the inner side of the drum *b*. The ring-piece *d* is not permitted to rotate upon *e*, but is prevented by means of a pin working in a slot. It follows that, as the taper plug *a* is turned, the ring-piece *d* is caused to move up or down, and its travel may be measured upon a scale at *f* (Fig. 137). This scale is so arranged that one division corresponds exactly to one whole revolution of *a*, the fractions of a turn being read off the divided drumhead at *g* (Fig. 137). This arrangement is common to all the adjusting plugs in Schumann's apparatus.

In the experimental work with the above apparatus it was necessary that the air layer between the source and the cover plate of the slit of the vacuum spectrograph should be as small as possible. In the case of the spark discharge Schumann succeeded in bringing the electrodes

within 1 mm. of the cover plate, this distance was therefore the total amount of air traversed by the rays. Photographs of the spark spectra of various metals were obtained in this way, but Schumann did not succeed in eliminating this air layer. The spectrum of the discharge through vacuum tubes was more easily obtained, since an "end-on" vacuum tube could be directly fitted against the fluorite cover plate of the slit. It was in this way that Schumann succeeded in reaching the limit of 1200 A. in the spectrum of hydrogen. Later, he dispensed with the fluorite cover plate, the vacuum tube being in connection with the whole of the apparatus. He found that no absorption was exerted upon the rays down to 1200 A.

The photographic plates used by Schumann in this work were prepared by himself, only very small quantities of gelatine being used. The special methods used by him in coating the plates will be described in Volume II., Chapter III.

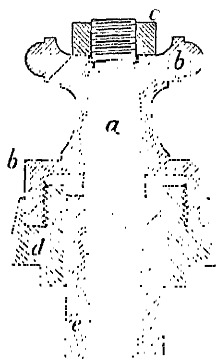


FIG. 136.

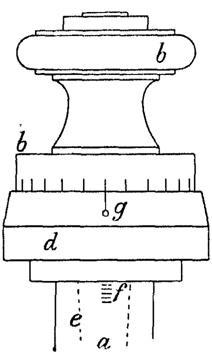


FIG. 137.

As already stated Lyman followed Schumann in the investigation of the short wave ultra-violet region and by the substitution of a concave grating for the fluorite prism was not only able greatly to simplify the apparatus but also to determine the wave-lengths of the lines in the new region. Lyman in his first important paper gives a detailed description of his spectrograph.[1] The apparatus consisted of two parts, the spectroscope itself and the receiver in which it was enclosed. The spectroscope was formed of a drawn brass tube 9·1 cm. in diameter, 96 cm. long and 1·5 mm. thick, one end of which was provided with an arrangement for holding the grating, whilst the other end carried the plate holder and the slits. The first grating had a radius of 97 cm. and 15,028 lines to the inch. The mounting is of the Eagle type since the plate is placed close to the slits, and the two slits and the plate lie on

[1] *Astrophys. Journ.*, **23**, 181 (1906); *Spectroscopy of the Extreme Ultra-violet*, Longmans, London, 1914.

the focal curve. The use of two slits is highly ingenious, since it enables the wave-lengths to be directly determined.

The vacuum receiver within which the spectroscope was placed consisted of a brass tube 11·3 cm. in diameter, 110 cm. long, and 1·8 mm. thick. Flanges were soldered to each end of this tube and the whole was closed by circular brass plates accurately ground to fit the flanges. The brass plate opposite the slits was pierced by two holes to admit the light and outside each of these was cemented the discharge tube. In these first investigations Lyman succeeded in measuring 300 lines in the spectrum of hydrogen, the shortest wave-length being about 900 A. Certain spark spectra were also measured.

By further improving his apparatus and by the use of the disruptive discharge in helium he succeeded in reaching the limit of 600 A. It may be noted that in these investigations Lyman did not work with his apparatus completely exhausted, but with the whole spectroscope and discharge tube, filled with the gas, hydrogen or helium, at low pressures. In his more recent experiments he substituted a grating of 50 cm. radius for the one he previously used and by employing helium at 1-2 mm. pressure he succeeded in extending the spectrum of this gas to 510 A., some evidence being obtained of a line at 450 A.[1]

In determining the wave-lengths of the lines in the hydrogen spectrum which served as standards in the Schumann region, two methods were used. The values of all the lines were first obtained by the two-slit method and these values were then checked by obtaining the stronger lines in the second spectrum and comparing their positions with known iron lines in the first spectrum. For this last purpose the first and second spectra obtained from the left hand slit were employed.

The theory of the two-slit method is briefly as follows—if two slits be placed on the circle, the diameter of which is the radius of curvature of the grating, the illumination of these slits by white light will give rise to two images, to each of which a set of spectra will correspond. For the present purpose it is sufficient to concentrate the attention on the two first spectra. It is evident that these two spectra will be shifted with respect to each other by an amount depending on the distance between the slits. If a photographic plate be placed between the two slits, and if the height of these slits be properly adjusted, one of these spectra will be superposed upon the other. At a given point on the plate, the light brought to focus from one slit will have a shorter wave-length than that from the other slit. If the sources of light be so selected that the wave-lengths in both spectra arriving at the given point have known values, then the shift of one spectrum with respect to the other may be determined by comparison of these values. If the apparatus is in adjustment both spectra are in focus upon the same circle, and the amount by which one spectrum is shifted over the other is a constant quantity, that is to say, if the shift is determined by

[1] *Astrophys. Journ.*, 43, 89 (1916); *Science*, 45, 187 (1917); *Nature*, 110, 278 (1922).

comparing known lines at one end of the plate, it must have the same value at the other end. It is upon this property that success in the use of the method depends.

The practical application of the method is as follows. The spectrum of iron was selected for comparison work. The grating was so turned that known lines in the spectrum of aluminium fell upon one end of the plate when the right hand or direct slit was illuminated by light from a spark between terminals of that metal. The shift of the principal spectrum with respect to the comparison spectrum was then determined by comparing the positions of these aluminium lines with known lines in the spectrum of iron. In order to insure accuracy this shift determination was recorded on the same plate as the hydrogen spectrum, the lines of which were to be measured. This was conveniently brought about by admitting the light from an aluminium spark directly through the discharge tube, for which purpose the tube was fitted with a window of quartz at the end not attached to the face plate. Upon the spectrum to be measured was superposed the comparison spectrum of iron, and in this spectrum fiducial lines were selected. The relative value of these lines was then obtained by subtracting the shift from their real value, previously corrected to vacuum. These relative values were then used as points of departure to determine the wave-lengths of the unknown gas spectrum. In practice the shift was 1180 A. so that the point in the iron spectrum falling on, say, $\lambda = 1400$ of the gas spectrum had a value of $1400 + 1180 = 2580$ A.

Owing to the dimensions of the plate only a region of about 760 A. can be photographed at one time. Thus, if the aluminium line at 1935·23 A. falls upon one extreme end of the plate, the other end corresponds to the wave-length 1175 A. In order to investigate light of a shorter wave-length than this value it is necessary to turn the grating, a process which necessitates a slight change in the adjustment of the slits and the plate.

To check the values thus obtained lines of short wave-length were obtained in the second spectrum. For this purpose the left hand slit was covered by a discharge tube without a window and the whole apparatus was filled with hydrogen as usual. Owing to the feeble character of the second spectrum only the stronger lines between 1550 A. and 1200 A. could be photographed. Their position was determined by comparison with first spectrum iron lines, obtained from light which had passed directly through the discharge tube. The average difference between the values obtained by the two methods was 0·3 A.

McLennan and Lang[1] have also carried out investigations in this region and observed the emission spectra given by the arcs of carbon, mercury, iron, copper, and zinc. The apparatus was in general design somewhat similar to that used by Lyman, that is to say, the Eagle mounting was adopted and there were two slits. The spectrograph was formed of a brass tube 115 cm. long, 15 cm. in diameter and 3·5

[1] *Proc. Roy. Soc.*, **95**, 258 (1919).

m. thick. At one end was a cover ground in and soldered, and at he other end a casting containing the slits and the film holder. In its eneral features this instrument and that used by Lyman were similar the one shortly to be described and a more detailed account is not ecessary. The grating had a radius of curvature of 120 cm. and o,000 lines to the inch.

The method used to find the wave-length of the lines observed was s follows. The zinc spark line $\lambda = 2026$ A. was obtained on a plate, nd its distance from the short wave-length end of the plate (which lways occupied the same position in its holder) measured. A mercury rc spectrum plate was then taken and the distance of the line $= 1849$ A. found from the end of the plate. Thus the distance etween the lines 2026 A. and 1849 A. was found. A large sheet of raph paper having one space for each Ångström and one for each illimetre dispersion was procured. The line $\lambda = 2026$ A. was given ero dispersion, and the line $\lambda = 1849$ A. gave a second point. A traight line was drawn through these points.

This graph was used to obtain the wave-lengths of all lines given ith this setting of the grating. The two carbon lines $\lambda = 1933$ A. and 348 A. were measured in this way. Then the grating was turned a ttle and another carbon plate taken, which contained these two lines mong others. The line 1933 A. was given zero dispersion, and the ispersion of $\lambda = 1348$ A. measured on this plate. A new straight raph was obtained having a slightly different slope from the last. gain the grating was turned, and this time the lines 1477 A. and 348 A. were used to get the new graph. Finally, for the last change of he grating the lines $\lambda = 1200$ A. and 1004 A. were used. This method, was realised, had some defects, but it is probable that it enabled the ave-length to be measured to within one Ångström.

The wave-lengths measured extended in the case of the carbon arc 584 A., whilst the spectra of mercury, copper, and iron did not exend beyond 1435 A., 1925 A., and 1427 A., respectively.

A very remarkable extension of the spectrum beyond the short ave-limit reached by Lyman has been discovered by Millikan and ndeed it would seem that he has succeeded in bridging the gap between he ordinary emission spectrum of an element and its X-ray spectrum. reliminary accounts of this research were published in 1918 and 1919, ut the work was interrupted by the war.[1] Recently, full papers have een published which contain a complete account of the results btained.[2]

The novelty of this work lies (1) in working in an essentially perfect acuum; (2) in using a source which consists of very high potential parks between electrodes set very close together; (3) in producing ratings of somewhat unusual properties, namely, properties which throw

[1] Millikan and Sawyer, *Phys. Rev.*, **12**, 168 (1918); *Science*, **19**, 138 (1919).

[2] Millikan, *Astrophys. Journ.*, **52**, 47 (1920); Sawyer, *ibid.*, **52**, 286 (1920); lillikan, Bowen, and Sawyer, *ibid.*, **53**, 150 (1921); Millikan, *Proc. Nat. Akad. ci.*, **7**, 289 (1921).

as much light of short wave-length as possible into the first order spectrum, and which have sufficient regularity of ruling to produce good images when the ratio of grating space to wave-length is as much as 70, instead of from 3 to 6, such as is common practice. The spectra were obtained by intermittent sparking between electrodes from 0·1 mm. to 2 mm. apart, with a battery of Leyden jars charged to potentials of several hundred thousand volts by a powerful induction coil. The gases evolved by the sparking render the attainment of this type of spark impossible after the pressure has risen above about 10^{-4} mm. Hence a mercury diffusion pump attached to the apparatus was kept in continuous operation, and the period between sparks rendered long enough to maintain the pressure at somewhat less than the above value. Although it takes at least a day to obtain a single plate, the actual time of sparking per plate is in general not over 30 minutes.

Some eight different gratings have been ruled and used, and the main lines checked upon several of them which possess different grating constants varying from 500 to 1100 lines per mm., so that the peculiarities of individual gratings have been altogether eliminated. However, it is clear that with a ratio of grating space to wave-length of as much as 70 in the case of the shortest wave-lengths obtained, the differences in the performance of different gratings are bound to be very marked. Although all of the gratings showed the same main lines in the region below 1000 A., two of them gave spectra greatly superior in distinctness and definition to those obtained by the others. The focal length of one of these gratings was 83·5 cm. and it had 505·3 lines per mm.

In the ordinary process of ruling gratings for work in the visible portion of the spectrum the surface of the grating is entirely cut away by the point of the diamond and the spectrum is produced by reflections from a series of new surfaces formed by the facets of the diamond. This in general throws the major portion of the light into a spectrum of higher order than the first, an indispensable condition for the high resolution upon which the excellence of a grating ordinarily depends. For work in exploring the extreme ultra-violet, on the other hand, the overlapping of spectra renders all spectra save that of the first order well-nigh useless, so that it becomes indispensable to throw the major portion of the light into that order.

It was soon discovered that gratings which were excellent for work in the visible and of which high hopes had been held for the new work were altogether useless. The expedient was therefore tried of ruling the gratings with a very "light touch" so as to leave a portion of the original surface functioning in the production of the spectra. If by such a procedure it were possible to cut away half the surface for example, the whole light would be thrown into the central image and into the odd orders in the intensity ratios 1, 0·4, 0·05, etc., the energy falling off as the inverse square of the order (always odd). The gratings with which Millikan succeeded in obtaining his shortest wave-lengths were ruled as nearly as possible in this way. On account of the necessity of leaving between the rulings a portion of the original surface no

rticular success has been gained in increasing the number of lines to e millimetre. The largest number has been 1100 per mm., the usual ımber being about 500.

Sawyer draws attention to a serious difficulty met with in eliminating e cause of a corrosion which was noticed on the grating. This rrosion was sufficient to cause marked discoloration of a new grating a single exposure and to diminish its power so that a few exposures ndered it useless. This situation made it impossible to get the best ults from a grating, even for a single exposure, and considerable time s spent in seeking the cause. From the fact that much of the dis- loration could be removed by wiping the grating with absorbent cotton oistened with a mixture of alcohol and ether, it was thought that the rrosion might be largely physical, caused by spattered particles shot from the spark. To test this possibility a pair of condenser plates re mounted just behind the slit with their faces parallel to the light am. This condenser was charged during the sparking to 1000 volts r mm. by a large storage battery. Very little material was caught the plates, however, and the corrosion still persisted. In order see if the effect was purely chemical, small mirrors of polished copper re placed in the spectrograph entirely out of the path of the light am. These mirrors became more heavily corroded than the speculum tal grating, indeed the film formed was sufficient for chemical analysis, ich showed that it was the sulphide produced apparently by the free phur and sulphur compounds present in the hard rubber insulation d rubber gaskets. The hard rubber insulation of the electrode- ıring conductors was replaced by redmonal or synthetic amber, pro- ced by the Redmonal Chemical Products Company of Chicago, and gasket rubber was replaced by sulphur-free antimony-cured gasket bber.

These changes made a great improvement. Not only was the rosion markedly reduced and the life of the grating lengthened in nsequence, but very much less gas was thrown off during sparking, ger series of sparks became possible, and a better vacuum was main- ned. A result of the better vacuum was the reduction of the fogging ısed by glow in the tube, and much clearer photographs were ob- ned. There still remained a slow corrosion of the grating due, obably, to very active gases, since these are known to be produced in antity by arcs and sparks in air. Frequent renewals of the gratings, refore, were still necessary, but conditions were much better than se that had existed earlier, and the extreme ultra-violet spectra were n obtained.

In the earlier experiments the following wave-lengths were recorded: ıc 317·3 A., iron 271·6 A., silver 260 A., and nickel 202 A. More ently Millikan records the fact that he has succeeded in photograph- the ultra-violet spectrum to as far as 136·6 A. in the case of minium and 149·5 A. in the case of copper. There is thus a gap resented by the factor 10 only between the shortest measured ultra- let rays and the longest X-rays measured by crystal-spectrometry,

which stops at 13·3 A. He found that the aluminium atom when excited by condensed sparks in vacuo emits no rays of wave-length between 144·3 A. and about 1200 A., where the M spectrum begins and extends with considerable complexity into the visible region. Optical spectra are therefore quite analogous to X-ray spectra in that large gaps occur between the frequencies due to the electrons in successive rings or shells.

As regards the photographic plates used in the above investigation, Lyman prepared his own by the method described by Schumann which will be given in detail in Volume II., Chapter III. McLennan and Millikan, on the other hand, used the plates now obtainable from Hilger which are prepared by a modification of the original process.

It is now possible to obtain a vacuum spectrograph which embodies the principles of construction adopted by Lyman and to a certain extent modified by McLennan. In this instrument the grating is mounted according to the Eagle method, two slits are employed, and the plate is placed immediately above the slits, the grating being slightly tilted from the vertical. The design of the instrument is very simple as it consists in the main of a wide metal tube with the two slits permanently fixed at one end, whilst the other end is fitted to a flange ground accurately flat at right angles to the axis of the tube. This end of the instrument is closed by a heavy brass plate ground to fit the flange and held in position by a gasket of soft wax, such as "sira" laboratory wax or Everitt's vacuum wax. The tube is 130 cm. long over all from slits to flange and is 30 cm. in diameter.

The grating, which is 101·5 cm. focus, has 596 lines to the millimetre and these are lightly ruled so as to throw as much of the ultra-violet light as possible into the first order, as explained above, the ruled surface being about 8 × 5 cm. It is mounted on a carriage which is provided with means for giving the grating a limited rotation about each of the three mutually perpendicular axes. The carriage can be moved along slides in order to enable the focus on the photographic plate to be accurately adjusted.

An external view of the apparatus is given in Fig. 138 which shows the two slits at the right-hand end of the instrument. These slits are recessed so that they lie on the focal curve of the grating and thus are necessarily of the fixed-jaw type. Each jaw is attached to a circular brass disc by two screws, the screw holes being slightly elongated to allow of the jaws being set parallel and the width of the opening being varied up to 0·5 mm. The brass disc is attached to the instrument also by two screws and again the screw holes are elongated to allow of the slit being set upright. The distance between the two slits is 5 cm., so that with one setting of the grating the range of spectrum is almost doubled, there being an overlapping of about 50 A. Either slit can, if desired, be covered by a circular brass plate held in position against the body of the apparatus by a wax gasket.

The focussing screw of the grating has eight threads to the inch. One division of the grating rotation drum moves the spectrum 9 A.

along the photographic plate, whilst on the photographs 6 mm. = 100 A., these latter data being of course only approximate.

The instrument carries a magnetically operated shutter which enables either two exposures to be made on one plate or the whole plate to be exposed at once. The shutter consists of a light aluminium vane

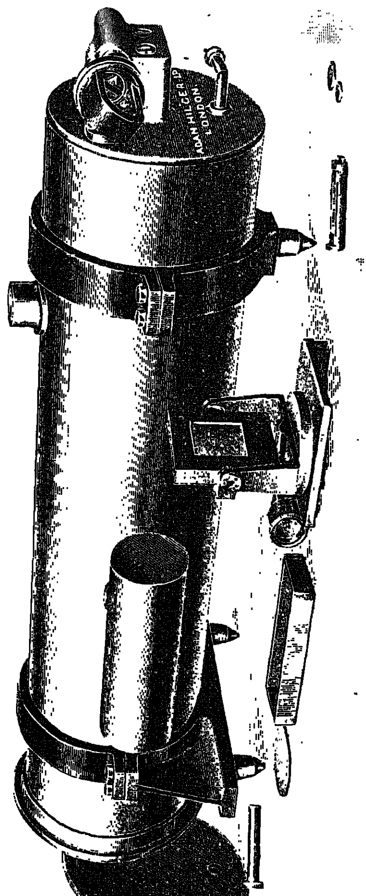


Fig. 138.

mounted internally close to the plateholder, and carrying upon its spindle an iron armature and a light pointer. The aperture through which this vane is introduced is closed by a glass plate hermetically sealed in, which provides an end bearing for the spindle when attracted by the magnet. The permanent horse-shoe magnet is mounted externally in a rotating collar and is shown in the illustration.

The plateholder and dark slide are of ingenious design which readily permits the introduction of the plate into the spectrograph in a fully lighted laboratory. The plateholder is cylindrical in form and will take a plate of 6 × 1 cm. which is bent by a small brass gate to the correct curvature. Specially thin plates will bear this curvature for several hours, although they are sometimes found broken when left in overnight. A metal handle about 10 cm. long is attached to one end of the plateholder and can be unscrewed from it when in position in the spectrograph. The plateholder is located in the spectrograph by a small key or feather to insure that the plate faces the grating. The dark slide consists of a metal cylinder with a keyway along its length into which the plateholder may be drawn as far as a stopscrew at one end. The other end is provided with a cup which fits over the circular opening of the plateholder aperture in the spectrograph.

The procedure of introducing a plate into the spectrograph is as follows: The handle is attached to the plateholder and the plate is clamped in position. The handle is then introduced into the cup end of the dark slide and the holder is pulled up to the stop. When the dark slide is brought out of the dark room it should be carried by the handle in order to prevent the plate from slipping out. When the cup is placed over the mouth of the aperture on the spectrograph, in the position determined by the screws-top, the plateholder can be introduced. The handle is then unscrewed and the aperture is sealed by a circular brass plate attached with a gasket of soft wax. The operation of withdrawal is of course the exact inverse of this.

The side chamber, one end of which is closed by a brass disc held against a flange by soft wax, contains a tray in which phosphorus pentoxide is placed. A plentiful supply of this drying agent is essential for attaining a good vacuum and it should not be allowed to become too moist. Frequent renewals are necessary and the instrument should be left exhausted as much as possible so as to guard against the formation of moisture films on the interior.

The large aperture above the instrument is provided for connection to the exhaust pump, whilst that in the large end cover plate is intended for the insertion of the focussing key during the adjustment. When the latter has been secured the key is removed and the aperture sealed with a small cover plate and soft wax. The tube shown under the slits is provided for connection to a vacuum-gauge or small discharge tube. If the latter is used the discharge should be passed as seldom as possible while the plate is in the instrument, since at certain stages of the exhaustion the discharge is liable to spread into the interior of the apparatus and cause fogging of the plate. If this aperture is not used it may be closed in the usual way with a brass plate and soft wax.

It is perhaps worth mentioning that a very convenient method of making the wax gaskets is to force the wax by means of a plunger through a hole 1·5 to 2 mm. in diameter. The plunger may be of wood and the outer vessel of brass, and except in very warm weather it is

recommended that the brass vessel be gently warmed near the small orifice when the wax will easily be forced through.

The connection to the exhaust pump should be as short and of as large diameter as possible. Any stopcock between pump and spectrograph should not restrict the connection and should have a bore of at least $\frac{5}{8}$ inch. An essential adjunct is a side tube to this main connection, provided with a stopcock, in order to admit air into the apparatus when required. In doing this care must be taken to admit the air very slowly so as not to disturb the phosphorus pentoxide.

For the exhaust pump a combination of Nos. 1 and 2 Trimount oil pumps is recommended. In Liverpool we have found the Cenco Hyvac pump very satisfactory, though not so rapid in its action. Since for work in the extreme ultra-violet a mercury vapour diffusion pump is essential there is no reason why a Geryk pump of the modern type made by the Pulsometer Company should not be used. These pumps have the advantage of being very quick in their action.

When this vacuum spectrograph is sent out from the makers it has been so adjusted that the aluminium line at $\lambda = 185\mu\mu$ falls about the centre of the plate when the right-hand slit is illuminated with the light from the aluminium spark. The adjustment must naturally be checked in case of alteration, which may be done as follows: The right-hand slit should be illuminated by an aluminium spark and a photograph taken. If the spectrum is not obtained on the plate it probably indicates an error in the inclination of the grating, that is to say, the spectrum falls either above or below the plate. A small adjustment should be made to the screw controlling the inclination and another trial made. This procedure should be continued until the direction and amount of adjustment necessary are determined. Any errors in definition may then be corrected by focussing and by setting the lines of the grating more parallel to the slit if necessary. If the grating be turned so that $\lambda = 200\mu\mu$ be at the right-hand end when the right-hand slit is illuminated, then the rays from $\lambda = 200\mu\mu$ to $\lambda = 125\mu\mu$ will be obtained with the right-hand slit and from $\lambda = 125\mu\mu$ to $\lambda = 50\mu\mu$ with the left-hand slit.

The method of wave-length determination with this instrument by the two-slit method has already been detailed in the account given of the investigation carried out by Lyman, to whom we are indebted for devising the method.

CHAPTER IX.

THE PRACTICAL RESOLVING POWER OF THE SPECTROSCOPE.

It was shown in Chapter III., p. 63 *et seq.*, how Lord Rayleigh deduced his well-known expression for the resolving power of a prism spectroscope. Lord Rayleigh found the relation

$$R = a\frac{d\theta}{d\lambda}$$

where R is the resolving power, a the aperture, and $\frac{d\theta}{d\lambda}$ the dispersion of the prism train. By the resolving power is meant the ratio $\frac{\lambda}{d\lambda}$, *i.e.* the ratio between the mean wave-length of a pair of lines that can just be resolved by the spectroscope and the difference in wave-length between the two components of the pair. It must be remembered that this refers strictly to an infinitely narrow slit, a condition that does not obtain in actual practice, and it is proposed to devote a short space to the consideration of the resolving power when the slit is given a definite width, as of course it must have under ordinary working conditions. It will be seen from what follows that the practical resolving power differs very considerably from the theoretical value with slit of infinitely narrow width, and since we are met with the fact that the giving of a finite width to the slit increases the amount of light available, and at the same time decreases the resolving power, we must, in designing any spectroscope, preserve the balance between the two best suited for the object in view. For this reason it is hoped that the inclusion of the following discussion of the contributory factors may prove of service. For this discussion we are indebted to Schuster, who first dealt with the resolving power of a spectroscope with slit of a finite width. The problem was then taken up by Wadsworth, who dealt with Schuster's equation and modified it to a certain extent. This modification Schuster has since shown is wrong, and in his last paper deals with the problem in the light of Wadsworth's criticism. Schuster only deals with the more or less simple case of a spectroscope with a slit of finite width, assuming that the spectrum lines to be resolved are infinitely narrow. This latter assumption, however, is known to be untrue, and Wadsworth has published a number of papers on the efficiency of the spectroscope in

which he takes both slit and spectrum line to have a finite width. Schuster, however, while not denying the utility of such investigations as these, points out that the resolving power of a spectroscope only depends upon the instrument itself. It is a question of slit width and dispersing train solely, and any discussion of resolving power should be rigidly restricted to these variables. For this reason, therefore, in the following pages the breadth of the spectrum lines will not be taken into account. At the same time the breadth of the spectrum lines must have a great influence, and for a full discussion of this reference may be made to four papers on the subject by Wadsworth.[1]

In his original article Schuster[2] found it convenient to introduce a new quantity which he called the "purity" of a spectrum, which was intended to serve as a measure of the efficiency of an instrument with wide slits, whilst the resolving power measured the efficiency with infinitely narrow slits. He showed that the purity P is given by

$$P = \frac{\lambda}{\lambda + d\psi} R,$$

where R is the resolving power, ψ the angle subtended by the diameter of the collimating lens at the slit, d the width of the slit, and λ the wave-length. Moreover, he showed that two wave-lengths differing by $\delta\lambda$ are resolved when $\delta\lambda = \frac{\lambda}{P}$.

Owing to the finiteness of light waves, each wave-length, even in a so-called pure spectrum, encroaches to some extent on a neighbouring one. In endeavouring to obtain a simple measurement of the encroachment Schuster neglected everything in the diffracted image beyond the first band. On this assumption each wave-length spreads over a certain finite range and not beyond. If 2ϵ be the width of the first band in the diffraction image of a narrow line, and σ the width of the slit image, each wave-length will spread through a distance of $\frac{1}{2}\sigma + \epsilon$ to either side of its centre. Two lines then will be completely separated when their distance apart is $\sigma + 2\epsilon$. Lord Rayleigh, however, has shown that they are distinctly resolved when their distance apart is only ϵ. Schuster then made the assumption that in the case of wide slits resolution begins when the distance between the lines is $\sigma + \epsilon$. The above equation was deduced under this condition.

Wadsworth criticised the above equation, showing conclusively that, owing to the rapid falling off of the light near the edge of the image of an extended luminous surface, the distance between the two lines at which they would be resolved is appreciably less than that given by the equation. In his later paper Schuster[3] accepts the major portion of this criticism and puts the following proposals forward.

[1] *Phil. Mag.*, **40**, 317 (1897); *Astrophys. Journ.*, **1**, 52 (1895); *ibid.*, 4, 57 (1896); *ibid.*, 3, 188 and 321 (1896).
[2] *Encyl. Brit.*, Art. *Spectroscopy*.
[3] *Astrophys. Journ.*, **21**, 197 (1905).

In the image of a very narrow slit at a distance ϵ from the centre the intensity of illumination is zero, whilst the intensity at a distance $\frac{1}{2}\epsilon$ is 0·40528 of that at the centre. It may, therefore, be said that the line spreads out on either side to a point which is at twice the distance of the point at which the intensity is equal to the above fraction. Let this definition be generalised as follows: the sensible image of a slit of finite width spreads through a distance δ to either side of its centre, such that the intensity at a distance $\frac{\delta}{2}$ is 0·40528 that of the intensity at the centre. Two lines at a distance of 2δ from each other may then be said to be completely resolved, but as a result of observation it is known that visual resolution begins when the distance apart is only δ. This distance Schuster adopts as the criterion of visual resolution. Now, if a point of the spectrum defined by λ be encroached upon according to the above definition by waves on either side as far as $\lambda + \delta\lambda$ and $\lambda - \delta\lambda$, then we may put

$$P = \frac{\lambda}{\delta\lambda}$$

and call P the purity of the spectrum. Two lines will be completely resolved when they are at a distance $\delta\lambda$, which is equal to $\frac{\delta\lambda}{P}$, and visual resolution will begin when their difference of wave-length is $\frac{\lambda}{P}$.

In the case of very narrow slits we have the same equations with the resolving power R in place of the purity P; the purity is proportional to the resolving power, but it also depends on the width of the slit. We may, therefore, put

$$P = pR$$

and call p the purity factor.

As Schuster points out, the above definitions assume a definite limit to which wave-lengths spread out on either side, and neglect all the light which may be beyond these limits. For narrow slits the neglected light is approximately that which lies outside the central diffraction image. Schuster gives a table showing the distribution of the energy of the light amongst the various diffraction bands, and shows that 90 per cent. is concentrated in the central band. A considerable amount of the light therefore is neglected in the above convention as regards the extent of encroachment, but, as is pointed out, this leads to no practical disadvantage, as the light so neglected is spread over a considerable range of wave-lengths, with the result that within any small range of periods the total energy is exceedingly small.

Schuster then calculated the distribution of intensity of light energy in the images of slits of finite widths, and the results are given in the table below. In dealing with the width of the slit it is an advantage to

express them all in terms of one convenient width called the normal width. In his investigation of the question of the deterioration of images owing to aberrations or other defects, Lord Rayleigh has generally admitted $\frac{\lambda}{4}$ as the limit of the allowable deviation from the ideal wave-front, if the image is not appreciably to suffer. Schuster, therefore, assumes that an extreme difference of path of $\frac{\lambda}{4}$ from one of the edges of the slit to the nearest and farthest points of the collimating lens will give images as good as if the slit were indefinitely narrow. He therefore fixes on this as being the "normal width," and his "slit factor" is the width of the slit in terms of this normal width. In the given table of intensity distributions the widths of slit σ are given in terms of the slit factor, and may be reduced to centimetres by multiplying them by $\frac{f\lambda}{D}$, where f and D are the focal length and effective diameter of the collimating lens, and λ is the wave-length. In the first column the distances from the centre are expressed in terms of the unit distance, viz. the half width of the central diffraction band in the focal plane of the telescope. These distances may be reduced to centimetres by multiplying them by $\frac{f_1\lambda}{D_1}$, where f_1 and D_1 are the focal length and effective diameter of the telescope lens, and λ is the wave-length.

Distribution of Intensity in Images of Slits of Finite Width.

Distance from centre.	σ = 0·0.	σ = 0·8.	σ = 1·6.	σ = 2·4.	σ = 3·2	σ = 4·0.	σ = 8·0.	σ = 12·0.
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·1	0·9675	0·9680	0·9695	0·9719	0·9752	0·9792	0·9999	0·9994
0·2	0·8751	0·8770	0·8825	0·8916	0·9040	0·9192	0·9983	0·9978
0·3	0·7368	0·7406	0·7518	0·7702	0·7954	0·8265	0·9917	0·9962
0·4	0·5728	0·5785	0·5956	0·6239	0·6627	0·7108	0·9753	0·9952
0·5	0·4053	0·4126	0·4345	0·4708	0·5209	0·5834	0·9441	0·9949
0·6	0·2546	0·2627	0·2872	0·3279	0·3845	0·4560	0·8946	0·9946
0·7	0·1353	0·1434	0·1676	0·2082	0·2652	0·3384	0·8252	0·9918
0·8	0·0547	0·0617	0·0830	0·1190	0·1705	0·2379	0·7374	0·9831
0·9	0·0119	0·0173	0·0336	0·0618	0·1030	0·1588	0·6356	0·9640
1·0	0·0000	0·0034	0·0138	0·0325	0·0610	0·1017	0·5261	0·9306
1·1	0·0080	0·0095	0·0143	0·0237	0·0395	0·0646	0·4166	0·8797
1·2	0·0243	0·0243	0·0247	0·0266	0·0320	0·0436	0·3146	0·8105
1·3	0·0392	0·0384	0·0362	0·0334	0·0319	0·0339	0·2261	0·7243
1·4	0·0468	0·0457	0·0427	0·0383	0·0338	0·0308	0·1550	0·6252
1·5	0·0450	0·0442	0·0420	0·0385	0·0343	0·0304	0·1027	0·5190
1·6	0·0358	0·0356	0·0349	0·0337	0·0321	0·0302	0·0681	0·4128
1·7	0·0230	0·0233	0·0244	0·0259	0·0274	0·0287	0·0481	0·3136
1·8	0·0108	0·0116	0·0139	0·0174	0·0216	0·0258	0·0387	0·2272
1·9	0·0027	0·0036	0·0064	0·0108	0·0162	0·0221	0·0356	0·1575
2·0	0·0000	0·0008	0·0033	0·0072	0·0123	0·0181	0·0352	0·1059

From the numbers in the above table Schuster calculated the factors of purity which express the fractions of the highest possible resolving power that are obtained under the different conditions of slit width. These values are given in the following table, which also includes a column (V.) showing the central intensities of the image in terms of the intensity with the normal width of slit, and a column (VI.) showing the same intensities in terms of the maximum intensity, *i.e.* that with an infinitely wide slit.

CONNECTION BETWEEN PURITY AND WIDTH OF SLIT.

I. Width of slit.	II. Slit factor.	III. Distance of resolution.	IV. Purity factor.	Relative intensities. V. Intensity = 1 for normal width.	VI. Intensity = 1 for infinite width.
0·0	0·0	1·000	1·000	0·000	0·000
0·1	0·4	1·002	0·998	0·406	0·100
0·2	0·8	1·009	0·991	0·805	0·198
0·25	1·0	1·014	0·986	1·000	0·246
0·3	1·2	1·021	0·980	1·191	0·293
0·4	1·6	1·038	0·964	1·558	0·383
0·5	2·0	1·060	0·943	1·902	0·467
0·6	2·4	1·089	0·918	2·217	0·545
0·7	2·8	1·124	0·889	2·500	0·615
0·8	3·2	1·168	0·856	2·751	0·676
0·9	3·6	1·221	0·819	2·967	0·729
1·0	4·0	1·283	0·780	3·148	0·774
1·2	4·8	1·438	0·695	3·415	0·839
1·4	5·6	1·624	0·616	3·571	0·878
1·6	6·4	1·823	0·549	3·646	0·896
1·8	7·2	2·022	0·495	3·670	0·902
2·0	8·0	2·221	0·450	3·674	0·903
3·0	12·0	3·214	0·311	3·789	0·931
D very large		D + 0·096		4·0689	1·000

A comparison of columns IV. and V. will help to determine the choice as to the width of the slit. For example, the normal slit width (slit factor = 1) gives a purity which is 1·4 per cent. less than the maximum possible. Nearly double the amount of light can be obtained by widening the slit until the factor is 2, and the purity only falls to 5·7 per cent. below the maximum. A gain of three times the light will mean a loss of about 20 per cent. of the purity, but a total intensity of 3·67 times that with the normal slit width is accompanied by a loss of just upon half the resolving power. Beyond this point a further widening of the slit greatly decreases the purity without much gain in the light.

The general conclusion gained is that in the case of spectroscopes which are designed for use with weak sources of light, they should be so made that the resolving power is about twice that actually aimed at.

The slit may then be set so that its factor is 7·2 which will give an intensity of 3·67 times that with the normal slit or $\frac{9}{10}$ths of the maximum possible, and a purity of about one half the theoretical maximum. Schuster goes on to say that the above calculations are based upon the supposition that the slit acts as a self-luminous source. In the laboratory this may be secured by the use of a condensing lens. The loss of light, however, may be very large unless the condensing lens subtends a much larger angle at the slit than does the collimating lens; in the case of the normal slit width it should be four times as great. If the slit have the width 8 the loss would not be great and so Schuster suggests the designing of spectroscopes with $2\frac{1}{4}$ times the required resolving power and the use of a slit factor of 8.

Morris-Airey [1] has pointed out that Schuster's expressions for purity do not appear to contain a factor depending upon the position of the grating or prism, but as a matter of fact the purity becomes greater as the angle of incidence of the light on the grating increases. When the slit has a finite width the light falling on the grating may be considered as a number of beams of parallel rays making slightly different angles with the normal to the grating. Let ϕ be the angle of incidence and θ the angle which the corresponding diffracted beam makes with the normal. Then if b is the grating space we have $b\,(\sin\phi - \sin\theta) = \pm\frac{n\lambda}{2}$ from which $d\theta = \frac{\cos\phi}{\cos\theta}\,d\phi$ and $\frac{d\theta}{d\lambda} = \frac{n}{2b\cos\theta}$, for any value of ϕ. The diffracted beams, therefore, make slightly different angles with the normal, the total variation being $d\theta$. This variation can be made as small as we please by increasing the value of ϕ. In the limit when the light falls at grazing incidence the different beams corresponding to any particular wave-length and order of spectra make the same angle with the normal and will be received by the telescope very nearly as if the slit had been very narrow. Again $\frac{d\theta}{d\lambda}$ is also increased so that the total effect is greatly to increase the purity. Morris-Airey points out that this result is really included in Schuster's formula, the term ψ has always been interpreted to mean the angle subtended by the collimator lens at the slit, but when the prism or grating is sufficiently tilted only part of the light passing through the lens is effective and it is only the width of this effective portion which should be considered in determining the value of the angle ψ. That angle, therefore, depends on the position of the prism or grating and may in the limit be reduced to zero. The smaller ψ is the greater is the purity, and ultimately by reducing its value the full resolving power is reached with a great width of slit. In fact, Morris-Airey finds that with a small grating of about 1300 lines to the inch it is easily possible to separate the D lines when the slit is half a centimetre wide. It must not be forgotten that the application of this is limited by the great loss of light by reflection when large angles of incidence are used.

[1] *Phil. Mag.*, **11**, 414 (1906).

AUTHOR INDEX.

SUBJECT INDEX.

19 *

H

I

L

M

S

T

PRINTED IN GREAT BRITAIN BY THE UNIVERSITY PRESS, ABERDEEN